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THE OPTICS OF THE NERVOUS SYSTEM*

By L. T. Troland

I. The Problem

The partition of the sciences one from another has in the main been determined by psychological rather than by physical criteria. As the strictly physical view of the world develops we see more and more clearly the physical irrelevancy of the sharp distinctions which were previously made between such sciences as mechanics, electrostatics and dynamics, the science of heat, chemistry, and even biology. It appears that the main subdivisions of science have been determined by different ways of sensing or perceiving the world rather than by any fundamental discontinuity in the world itself.

However, the various modes of acquaintance with the world are themselves legitimate topics for scientific inquiry. Such studies belong, strictly speaking, to psychology, but there are certain branches of physical investigation which have so intimate an association with particular senses that it seems quite artificial to divorce them. Perhaps the most striking example of this sort is our own science of optics. Not only is the word optics derived from Greek roots signifying the eye, but the historical development of the science has virtually been an attempt to understand the process of vision in all of its aspects. The paths of optical investigation have developed from the eye as a starting point. Our original knowledge of short wave radiant energy was restricted to light, which we now define with explicit reference to the reactions of the retina. The extension of the spectrum on either side has rested mainly upon the introduction of artifices by which an indirect visibility, such as that attained through the photographic

* Presidential Address, Optical Society of America, October 26, 1923.

plate, could be given to ultra-violet and infra-red. Most of us are willing to admit the visually demonstrable X-rays into the domain of optics, but we would rule out the Hertzian waves which from a physical standpoint are equally homogeneous with light, the latter being demonstrated mainly through the auditory sense. Optical instruments, with the properties of which so large a part of optics is concerned, are in nearly all cases subservient to the eye, being so many different appliances for extending the range of vision.

The expansion of optical research from the eye as a starting point has taken place mainly outward from the retina into the great world of space which lies before it. The purpose of the present paper, on the other hand, is to deal briefly with a department of optics which develops by an expansion from the retina inward through the nervous system and ultimately into the realm of consciousness. If our purpose in general optics is to understand all facts which are relevant to the act of seeing, then these post-retinal processes are equally important with the pre-retinal ones. We can see much better without light than we can without an optic nerve, and we can see *more* without both light and an optic nerve than without a brain. The ancient Greeks recognized the dependency of vision upon emanations from the environment and also upon what we now call the optic nervous system. Since their time tremendous strides have been made in our knowledge of the optics of the environment, but relatively little progress has been achieved in our understanding of the even more important processes which constitute the optics of the nervous system.

The last mentioned line of investigation is not synonymous with physiological optics, although naturally it forms a subdivision of the latter. Physiological optics may be said to deal with all phases of vision which occur within or depend directly upon the living organism, and the clearest chapters of physiological optics are those which relate to the non-nervous functions of the eye. Physiological optics may be said to begin at the cornea and to end at the ocular musculature or other motor mechanisms regulated by vision. Psychophysiological optics carries over from these considerations to consciousness. The optics of the nervous system is concerned only with that portion of these activities which begins at the retina and ends at the motor nerve terminations, or in consciousness.

Nervous optics, thus defined, is marked off from the remainder of optical science, whether physiological or environmental, by a qualitative gap much wider than that which separates the optics of the eye

from that of other optical systems. It is evident that physiological optics from the cornea to the retina deals with materials and laws essentially similar to those which are involved in the study of cameras, telescopes or microscopes. Radiant energy behaves within the media of the eye just as it does in glass. When it reaches the retina, however, it is transformed into quite a different kind of energy, which undoubtedly obeys laws dissimilar to those of ordinary optics. Nevertheless, some degree of continuity must exist between the pre- and post-retinal activities; otherwise vision would be unable to give us accurate information concerning the objects before our eyes. The extension of the conception of optics to include the visual nerve processes is justified not only by etymology and by history but by certain fundamental analogies which we shall now briefly consider.

Firstly, nerve optics, like general physical optics, is concerned with the *propagation* of a continuous influence from one point to another through space along a definite path and at an approximately constant velocity. Secondly, the distribution of the nervous disturbance, like that of radiant energy, is *quantumhaft* both in the direction of propagation and at right angles to it. Thirdly, *images* or characteristic configurations of the disturbance both qualitative and quantitative exist in both cases. Fourthly, in both instances these configurations are progressively modified as a consequence of differences between the successive layers of transmissive or reflective media through which they pass.

If we were to be logically puristic we could not include under the optics of the nervous system any considerations of consciousness or of purely introspective data. However great may be the differences between the events occurring in living and in non-living matter, they may nevertheless be conceived as being fundamentally homogeneous. The substance of a nerve cell is just as reducible to ultimate physical units, such as protons and electrons, as is that of a glass lens. Not so, however, with the facts which we call conscious or introspective. The visual objects compounded of colors in perspective space which exist in our experience in every complete act of vision are composed neither of nervous nor of any other species of matter. No one has ever been able to give the slightest suggestion of a plausible reduction of such objects to physical terms. Radiant energy is one thing, the nerve impulse another, and color quite a separate third entity. Yet in spite of this discreteness of the physical and the psychological, important similarities exist between them and their interdepen-

dencies are so thoroughgoing that they form a single mathematical or functional system. Moreover, the act of vision as we ordinarily conceive it involves the psychological facts just as much as it does the physical facts in the case. For these reasons we are justified pragmatically in extending our notion of the optics of the nervous system so that it embraces the determination of images (including perception and sensation) in consciousness by the corresponding processes on the physical side.

Our problem accordingly shapes itself somewhat as follows. To give an account of the details of the visual process, beginning with the excitation of the retina and ending, let us say, with the visual object as it appears in the consciousness of the observer. We can hope in a brief discussion such as the present one to consider this difficult problem only in a broad way, indicating the most general principles which are involved and summarizing the established facts in a general manner.

II. THE OPTICS OF THE RETINA

The body of the eye with all of its various refracting media, although a sensory device, is not technically a portion of the nervous system. This statement depends not only upon an examination of its inherent properties, but upon its *embryological development*, in which the retina and optic nerve are formed as extrusions from the brain, while other portions of the eye are derived from non-nervous germinal tissues. The "optics of the nervous system" thus begins with the receptor processes of the retina, concerning which we know so little although concerning which we have speculated so much. It is far from being my desire to propound any new hypotheses regarding the retinal reaction. Nevertheless, in order to develop concretely the problem which we are considering it will be necessary to make some assumptions relating to the nature of the retinal process.

The study of the optics of the retina, or of any other portion of the nervous path, naturally divides itself into two parts dealing, firstly with the *nature* of the processes at any single point, and secondly, with the *arrangement* of the processes at different points to form *images*. We must begin, of course, with the fundamental idea of the "duplicity theory" that the retina contains two distinct kinds of receiving elements, the rods and the cones, the former sensitive to lower and the latter to higher intensities of the radiant stimulus. The cones, moreover, are specifically sensitive to wave-length composition, giving rise to nerve

currents which are differentiated with respect to wave-length as well as stimulus intensity, this property being absent in the case of the rods.

The recent researches of Hecht[1] have greatly strengthened our belief that the first step in the response of the rods consists in the photochemical decomposition of the visual purple pigment which they contain. Other studies by the same investigator[2] have indicated that, at least in the case of molluscs, the first step is the production of a catalyzer which controls the velocity of a second chemical reaction which in turn determines the nerve current, as demonstrated in movement or consciousness. The extreme energy sensitivity of the rods in the higher animals suggests strongly that this catalytic mechanism is likewise a feature of their response.

The manner in which the catalyzed reaction sets up the optic nerve current can readily be conjectured. We know from experimental, as well as theoretical considerations, that the nerve current consists of a series of electrical pulses, travelling along the individual nerve fibres, and that the effect of the stimulus upon the retina is to increase the electrical negativity of the retinal receiving cells. I have elsewhere described a mechanism by which an increase in the ionization of an electrolyte[3] contained in the receptor cells will bring about a corresponding increase in their electrical negativity and a resulting increase in frequency of the nerve pulses, so that the number of these pulses passing a given point in the nerve path per second represents the *intensity* of stimulation. This mechanism rests upon the principle that the receptor cells are negatively polarized, whereas the conducting units bear a positive polarization, the resulting depolarization which occurs at their junctions being the condition of the nerve impulse generation. An alternative possibility, also consistent with the modern theory of the nerve current,[4] is that the augmented negativity

[1] Hecht, S. The Dark Adaptation of the Human Eye. Journ. of Gen. Physiol., *2*, pp. 409-517; 1920.

The Photochemistry of the Visual Purple. Journ. of Gen. Physiol., *3*, pp. 1-13; 1920.

The Visibility of Monochromatic Radiation and the Absorption Spectrum of the Visual Purple. Journ. of Gen. Physiol., *5*, pp. 1-33; 1922.

[2] Hecht, S. Sensory Equilibrium and Dark Adaptation in *Mya arenaria*. Journ. of Gen. Physiol., *1*, pp. 545-558; 1919.

The Nature of the Latent Period in the Photic Response of *Mya arenaria*. Journ. of Gen. Physiol., *1*, pp. 657-666; 1919.

[3] Troland, L. T. The Nature of the Visual Receptor Process. This Journal, *1*, pp. 3-15; 1917.

[4] On the modern theory of nervous activity, see: Troland, L. T., The Physical Basis of Nerve Functions. Psychol. Rev., *27*, pp. 323-350; 1920.

of the receptors arises from a decrease in the permeability of their enveloping membranes, this change in the nature of the membrane actually constituting the second, or catalyzed process of Hecht's scheme. Increased negative polarization could also follow immediately as a consequence of a photo-electric emission of electrons by the visual purple, if these electrons possessed sufficient speed to send them through the membrane.

Any one of these conceptions is capable of furnishing us with a clear picture of a possible process by which the action of radiant energy upon the retinal rods can be translated into a nerve current varying in degree with the stimulating power (or light intensity) of the incident energy. The case is quite different, however, when we come to consider the cones. The accepted principle that the individual nerve pulses cannot vary in magnitude or form—the "all or none" principle—forces us to transmit intensity in terms of impulse frequency or density, and no medium seems to be left to carry the remaining two variables or determinants which are absolutely required by the facts of trichromatic vision. Recent studies by Adrian and Forbes[5] indicate clearly that the all or none principle applies to sensory as well as to motor nerves, and I have elsewhere[6] presented measurements which specifically associate this principle with the human optic impulse. In this situation I see at present only two alternatives. The first is that there are actually three different kinds of cones, connected separately to higher nervous centers, our inability to detect their existence by tests with fine color patterns being due to the fusion of adjacent chromatic processes, while the corresponding intensity aspects of the excitation remain spatially distinct. The second alternative is that the stream of "all or none" pulses which carry the intensity factor in rod and cone fibres alike are *modulated* in the latter in such a manner as to convey two additional chromatic factors.

I use the term "modulation" here in a sense analogous to that in which it is employed in the theory of the radio-telephone, involving the impression of a low frequency variation upon the medium provided by a higher frequency oscillation. In the case of the nerve impulse, however, such modulation could not be continuous or smoothly graded, but would necessarily follow the all or none principle, and would consist

[5] Adrian, E. D. and Forbes, A. The All-or-Nothing Response of Sensory Nerve Fibres. Journ. of Physiol., *56*, pp. 301-330; 1922.

[6] Troland, L. T. The "All or None" Law in Visual Response. This Journal, *4*, pp. 160-185; 1920

in the introduction of variable gaps into an otherwise uniform sequence of pulses. Two independent modes of variation could exist very simply if the lengths of the gaps and of the filled intervals, respectively, were separately regulated. Many other systems of modulation are conceivable and it would be folly for us to attempt to decide between them until we can arrive at some definite conception as to how the modulation can be controlled by wave-length composition. Such control of modulation I should be inclined to assign to the second reaction of Hecht's scheme, supposing that this is separately affected by wave-length composition in the case of the cones, but not in that of the rods. If we accept the suggested interpretation of this reaction as a membrane process, we may note that the latter is peculiarly fitted to control the rhythm of the neural disturbance.

The general form of the system thus outlined harmonizes with the facts to a considerable degree. It makes it possible for the primary excitation mechanism to be the same in both rods and cones, being in both the basis of luminosity, brilliance or the intensity factor. The recent studies of Hecht, demonstrating the close similarity in form between the rod and cone visibility curves, suggest that the latter depends upon an extremely dilute visual purple suspended in a medium optically more dense than that of the rods. Extant psychophysical data indicate that the chromatic aspect of vision is due to processes superimposed upon those underlying the achromatic aspect, rather than *vice versa*, as more commonly conceived. The three-fibre hypothesis, on the other hand, is still not entirely dead. Furthermore, an intermediate system is conceivable, involving only two sets of cone fibres, with a single form of modulation in each. This possibility has properties which make it decidedly interesting, but time will not permit me to develop its details here.

Let us turn now to consider some necessary features of the retinal process, regarded as an *image* or as an optical form. It must be remembered that the retina is not merely a receptive device, but constitutes within itself, an elaborate system of conductors.[7] The image of radiant energy, which is focused upon the receptor layer by the refractive media of the eye, passes through these conducting elements on its way, but presumably does not affect them directly. The influence is, so to speak, reflected back upon the conductors at the receptor stratum,

[7] On the anatomy of the retina, see: Schäfer, E. A. *et al*, Quain's Elements of Anatomy. *3*, Part 2, pp. 225-242; 1909.

changing immediately upon such reflection from electro-magnetic waves travelling 186 thousand miles a second into ionic pulsations in minute nerve fibres, propagated only a hundred feet per second. The radiant image within the retina clearly must have the general form of a hemispherical shell, somewhat roughened in texture by the optical irregularities of retinal topography. Within this shell are represented point for point those superficies of external objects which are turned towards the eye, the representation being inverted with respect to the object. The mosaic of rods and cones is sprinkled throughout this radiant image, densely at the center but more sparsely towards the periphery, and being absent entirely at the optic disk, or the place of exit of the optic nerve. Accordingly, when the visual disturbance starts on its path along the retinal conductors, it has the form of an irregular screen-plate reproduction of the radiant image, certain portions of the latter failing of representation.

The radiant retinal image, although far from being a perfect depiction of the external object, nevertheless bears a close resemblance to an inverted geometrical projection of the latter upon a curved surface. It has approximately the distribution of intensities and wave-length compositions which are characteristic of the object surfaces directed towards the eye. The receptor process image and the resulting nerve current image in the external and the middle segments of the rod and cone cells, respectively, have a generally similar form, except for the lacunae introduced by the discreteness of the sensitive elements. Intensity and wave-length have been translated at each point into specific photochemical effects or into nerve pulse frequency and modulation of the same. In these terms the neural image still has a recognizable semblance of the original object, but as the currents in five million cones and a hundred million rod fibres travel radially inwards, the image structure begins to change. In the region of the fovea, when the internal segments are reached, the densely packed currents of the central retina disperse laterally. Elsewhere they suffer local condensation as the excitations of numerous rod or cone cells converge upon a single bipolar cell, the next ensuing conducting element. This condensation is further continued at the next level of conduction transfer, when the nerve currents pass from the bipolar cells to the ganglion cells from which emanate the fibres of the optic nerve. In the extremely short path of less than one-half a millimeter, the number of conducting elements is decreased from over a hundred million to about half a mil-

lion, which is approximately the number of fibres in the individual optic nerves.

This convergence of adjacent currents into common paths reduces the representation of rod response much more than it does that of the cones. More than twenty rods may contribute to only a single optic path, whereas all of the foveal cones are provided with "private lines." Thus the mosaic conduction image shrinks concentrically, the intensive and qualitative aspects of the peripheral points being averaged, while the details of the central region are preserved and form an increased fraction of the whole. This is the state of affairs while the nerve currents are still moving perpendicularly in the retinal shell, and when the *neural image*, (or nerve image)—if such we may call it—still has some geometrical similarity to a projection of the external object. When the ganglion cells have been passed, however, the entire image abruptly shrinks along the inner surface of the shell, its area being reduced from about eleven hundred square millimeters to a little more than eight square millimeters. In this shrinkage, special regions of the image undergo peculiar distortions. The elements derived from the fovea move towards the exit of the optic nerve in arc-shaped paths, which are more bowed for the temporal than for the nasal sides of the fovea, and there are local segregations or clottings of adjacent excitations all over the field, corresponding to the bundles of nerve fibres which form an interlaced net-work on the inner surface of the retina.

As it travels over the retinal surface the image due to any single instant of stimulation may be regarded as a series of concentric circles contracting at uniform speed around the exit of the optic nerve. The points nearer the latter reach and enter it sooner than those which start further away, so that within the nerve the image must be drawn out into a long, narrow, cone-shaped surface with its apex turned in the direction of travel. When the apex of this cone has reached the optic *chiasma* the hindmost portion, representing the temporal (or external) peripheral retina, has only just entered the optic nerve. Cross-sections of the optic nerve conduction therefore do not represent simultaneous conditions at the corresponding object points.

III. THE OPTICS OF THE OPTIC NERVE AND TRACTS

Within the optic nerve the neural image broadens out again slightly so that its cross-section has perhaps four times the area which it

possessed at the point where the nerve passed out of the eye-ball. The individual active points of the image are correspondingly dispersed. Although still greatly condensed in comparison with its retinal magnitude, the image may even now retain a vague resemblance to a geometrical projection of the external object upon the nerve cross-section—or upon the conical surface just mentioned if an instantaneous stimulus is considered. Close to the exit of the nerve, however, the fibres from the retinal center are naturally displaced to that side of the nerve bundle which is nearest to the fovea. However, they quickly migrate again to the center of the transmission system. This is in preparation for the partition of conductors which occurs at the optic chiasma.

The chiasma is a place of physical conjunction of the two optic nerves. There is, however, no fusion of the nerve currents from the two retinas at this place, but merely a regrouping of the conducting elements, as follows. The image derived from each eye is split sharply along a line corresponding to the vertical of each retina, with the exception that the most central image elements—corresponding to the two foveas—are divided so that there is a uniform representation of the foveal areas in each of the divisions of the nerve current. As the neural image passes through the chiasma, the portions corresponding to the right-hand sides of the two retinas enter the right optic tract, which is to carry them to their destination on the right cerebral cortex, while those corresponding to the left-hand sides of the retinas similarly enter the left optic tract. Foveal elements, representing both halves of both foveas, enter both tracts.

Just beyond the chiasma, the geometrical resemblance of the nerve images to the original retinal image must be quite vague. The binocular image is split between the two diverging optic tracts, the right hand portion of the visual field having a double representation in the left tract, and the left-hand half of the field being dually represented in the right tract. In each tract there are essentially duplicate representations of the entire foveal field. According to the results of Williamson and of Henschen,[8] the fibres of each tract which come from the eye on the same side (uncrossed fibres) occupy the center of each tract, while those from the other eye (crossed fibres) surround them, being somewhat denser below than above. Thus, in the tracts, at least before any visual brain centers are approached, neural image points which correspond visually are not yet contiguous, but the images

[8] See Quain's Elements of Anatomy, *3*, Part 1, p. 239; 1908. Also refer to this work for a discussion of the anatomical connections of the visual conductors.

for the same right and left eye half-fields retain their individuality to some degree, the one being wrapped around the other. At the same time, representations of the two half-fields, right and left for either eye (excepting the foveas), are being carried to opposite sides of the brain. It seems very doubtful whether from the pattern of excitation in this system we could learn anything concerning the pattern of the retinal image or stimulus, without using an elaborate physiological key. Yet it is certain that the excitation pattern in question carries to us all that we ever know through vision, of the stimulus and the world of objects outside.

The next phase of the conduction, on either side of the head, is the emergence of the visual image impulses from the continuous conductors in which they have thus far travelled from the ganglion cells of the two retinas. Just before this occurs each tract divides into two branches, one of which turns inwards towards the center of the brain while the other continues along the outward or lateral course. The two inward branches lead to two symmetrically placed nerve centers called the anterior quadrigeminate bodies, while the two outward branches carry the currents to similarly symmetrical centers known as the external geniculate bodies. It appears that both the inner and the outer systems of conducting paths must receive at least a diluted or rarified representation of the whole visual image. However, only the external system is concerned in the propagation of the image to the cerebral cortex, and hence—it appears—in the determination of visual consciousness. The inner system provides a basis for automatic ocular reflexes, such as the constriction of the pupil, without intermediation of the cortex or the necessary presence of consciousness.

In the external geniculate bodies the neural images of the half-fields and fovea, on either side, are transferred across junction points or nerve contacts to a new set of conducting fibres. Von Monakow believed it impossible that in this transfer the individuality of the impulses in the separate fibres could be preserved, but subsequent investigations have shown that he was wrong. There is now not the slightest doubt that the pattern of the neural excitation beyond the geniculate bodies has as specific a dependency upon that of the retina as is the case for the pre-geniculate conduction.[9] It appears that in

[9] See, e.g., Best, F. Zur Theorie des Hemianopsie und der höheren Sehzentren. Arch. f. Opthalmol., *100*, pp. 1-31; 1919.

Also: Monbrun, A. Le centre cortical de la vision et les radiations optiques. Les hemianopsies de guerre et la projection rétinienne cérébrale. Arch. d'ophtalmol., *36*, pp. 641-670; 1919.

the geniculate bodies the lines of conduction from the two retinas become more or less regularly mixed, so that optically corresponding points of the two are represented by conducting points spatially close together, although still without fusion or "short-circuiting" of the two lines of transmission. This pairing up of the fibres probably starts in the optic tract, so that at and near the geniculate bodies the upper quadrants of the retinas on the same side are represented by the upper portions of the tract and geniculate bodies, while the lower quadrants are linked with the lower parts of the same nervous organs. Here then we find a tendency towards the reconstruction of the retinal image, but one in which both the right and left eye representations are systematically interwoven. The entire representation of the binocular field is still, with the exception of the foveal region, cut into two separate, vertically delimited halves, which have no physiological connection at this level of the conduction.

Beyond the geniculate bodies, the two composite half-images are transmitted along the central visual tracts, on either side, to be "projected" upon the inner surfaces of the two cerebral hemispheres, respectively. On account of the manner in which the conducting fibres flare towards the ends of the paths, their structure is known as the "optic radiation." Considerable dispute exists concerning the exact course and identity of the optic conductors, but the most recent opinions—based upon many studies of war injuries to the brain—lead to the following account.[10] Each neural half-image is carried in a band of fibres, at first forming a single compact bundle, which is about a centimeter high by half a centimeter in width, the conduction first curving outwards and then inwards again through the cores of the two respective cerebral hemispheres, seeking circuitously its destination within the lower, back portion of the head, in the so-called occipital lobes. On either side the upper layers of fibres carry the image elements derived from the upper quadrants of the same side of the retinas, while the lower layers correspond similarly to the lower retinal quadrants. Similarly situated points on the retinal areas are represented by physically adjacent processes in the visual tract conduction.

The exact destination of the impulse images lies in brain surfaces which center about a deep indentation of the cerebral cortex known as the calcarine fissure, which exists in duplicate in the two hemispheres.

[10] See Monbrun, *loc. cit.* Also, on connections of the macula: Morax, V. Discussion des hypothèses faites sur les connexions corticales des faiseaux maculaires. Ann. d'oculist., *156*, pp. 25-35; 1919.

When the conducting fibres approach the neighborhood of this fissure they split into two separate bundles, corresponding to the upper and lower retinal quadrants on the respective sides, one bundle distributing its impulses on the upper face of the fissure—which is essentially horizontal in direction—while the other supplies the lower face. Currents from the peripheral portions of the retinal field arrive at forward regions of the fissure, those from central retinal points being carried further back. The currents from corresponding points on the two retinas are still physically contiguous. The similarity between the neural and the retinal images is now once more quite remote, the former having been broken into four parts, the portion corresponding to the center of the retina having been pushed to one extremity and being greatly expanded relatively to the parts representing the peripheral retina.

IV. THE OPTICS OF THE CEREBRAL CORTEX

For purposes of imagination the cerebrum, the portion of the brain which is principally concerned in the higher psychological activities such as visual perception, may be compared to the kernel of a walnut, (although it is doubtful whether an accurate anatomical knowledge is at the basis of current colloquialisms.) The two halves of the kernel, with their plane of separation placed vertically, represent the two cerebral hemispheres, while the surface irregularities may be compared with the convolutions and fissures of the cerebrum. Now the portions of the cerebral cortex—or "cerebral skin"—to which the optic impulses are conducted, lie mainly upon the surfaces which face one another at the plane of separation, rather than upon any surfaces which are exposed when the hemispheres—the two halves of the kernel—are together. The optic areas, however, are not for the most part parallel to the separation plane, but are pressed outwards in opposite directions into the bodies of the two respective hemispheres, by deep fissures which lie roughly in a horizontal plane in either hemisphere. The visual portions of these *calcarine* fissures, as they are called, are each about two inches long and three-quarters of an inch deep at their deepest parts. The visual area proper extends also somewhat beyond the region of the fissure at the rear, so that a relatively small section lies upon the outer surfaces of the two hemispheres. The exact shape of the hemispheres and also the precise form of the area which receives the optic impulses varies appreciably from individual to individual.

As already suggested, the distribution upon the two calcarine surfaces, of the neural image derived from the two retinas, is approximately as follows. In the first place, with the exception of the foveal regions, the left halves of *both* retinas are represented upon the left hemisphere only, while the right halves of both retinas similarly are connected with the right hemisphere alone. Corresponding retinal points are represented by closely adjacent nerve cells in the same hemisphere. Considering, now, a single hemisphere of the pair, the deepest portion of the calcarine fissure corresponds to the retinal horizontal axis, the forward points being associated with the retinal periphery, while the rearward points are linked with the more central regions of the retina. The lower surface and lip of the fissure correspond with the lower quadrant of the same half of both retinas, and the upper surface and lip are connected with the upper retinal quadrants. The foveas are doubly represented on the extreme rear poles of the two hemispheres, outside of the fissures. Next in advance come the outlying central, or macular, regions, extending into the fissure, and then progressively more peripheral zones until the extreme periphery is reached at the most anterior section of the fissure. As is to be expected from the functional importance of the fovea, as well as its fine-grained retinal structure and exclusive nervous connections, the cerebral areas representing it and adjacent central zones of the retina are greatly expanded relatively to those representing peripheral retinal zones.

Although the optic neural image, as thus projected upon the cerebral cortex, has a geometrical form and pattern markedly different from that of the retinal image, it may nevertheless be conceived as derived from the latter by a process of folding and local expansion or contraction. Except for the splitting of the retinal field vertically between the two hemispheres, adjacent retinal points can be represented generally by adjacent cortical points, so that however much distorted, the continuity of the half-image is not broken. The known facts do not definitely establish this continuity, but they are consistent with it, although suggesting some segregation of central (macular) as opposed to peripheral zones. The two half-images, however, remain completely without neural interconnection at this level of the conduction, being localized in physiologically separate organs, the right and left hemispheres, respectively.

It is now a principle beyond dispute, proven by the rich data provided by war injuries to the cerebrum, that there is an approximate point-to-point representation or transfer of the double retinal image upon the

cerebral cortex; and consequently that definite patterns of excitation upon the retina must normally result in equally definite excitation patterns upon the cortical surface. Limited injuries to the visual cortex produce artificial blind-spots, or "scotomas" which are clearly defined in outline and within which—so long as the lesion persists—there is no recovery of vision. These spots are of the same size and shape for both eyes. Complete destruction of the visual portion of a single hemisphere causes total blindness on one half of the visual field—except for the small foveal indentation—the vertical line of demarcation between vision and non-vision being very sharp.

When we try to imagine the intimate nature of the processes which form the cortical image, we are of course forced to think of what we know concerning the nerve impulse. We can feel sure that the cortical process is essentially an electrical disturbance, involving the displacement of ionized particles through the substance of semi-permeable membranes. The currents arriving at the cortex must consist of a series of pulses of such activity, and we may suppose—in harmony with what has previously been said—that stimulus intensity is represented at each point by the temporal frequency of these pulses. Chromatic characteristics may depend upon different forms of "modulation" of the fundamental intensity pulsation, as already suggested. The image form is created by the manner in which these characteristic activities are distributed over the cortical surface, as determined by the incoming currents.

Although we tend to think of the cortical projection areas as termini of conduction, they are in reality only way stations in a continuing process of propagation. Anatomically, the cortex consists of stratified neural conductors, forming a complicated net-work. The visual projection area is characterized by the presence of a marked striation which is absent elsewhere, and which must have some special significance for the visual function, although not one which we are able at present to explain. From the projection areas the optic neural currents are propagated to even higher cerebral centers, concerning the processes within which we know very little in terms of pure physiology, but the psychophysical significance of which is fairly clear.

V. THE OPTICS OF CONSCIOUSNESS IN RELATION TO THE NEURAL IMAGE

The most fascinating aspect of the general problem which we have before us is undoubtedly that of the relationship holding between

the optic neural image and the visual image in consciousness. The latter image—the psychological reality—is nothing less than the whole visual object of common-sense experience, compounded of color and the perspective properties of visual space, and being quite distinct from the physical object—composed of electrons and protons—which lies before the physical eye. This visual object, quite evidently, is localized at no place along the path of optical nerve conduction, yet its existence depends upon that of the conduction processes; some of them if not all.

As naïve philosophers-in-the-street, we tend to associate the visual objects of our immediate experience directly with physical objects or "objects of vision." However, experiment shows that an interruption of the physical and physiological propagation of the visual influence anywhere from the physical object to the cortical projection areas—and beyond—leads to modification and usually to the annihilation of the *visual* object. The blindness resulting from cortical injury is even more complete than that which accompanies the absence of light or the loss of both eyes, since frequently in the first instance one loses the power even to *imagine* things visually. This is not the case, however, when the lesion is confined to the visual projection areas and does not involve later phases of the conduction, a fact which indicates that the determination of the visual object goes beyond the projection mechanisms to higher cortical centers. It appears, furthermore, that these higher centers are capable of arousing visual objects without the assistance of any lower nerve path activities, since the occurrence of visual hallucinations within a cortically conditioned blind-spot is a common phenomenon. Such hallucinations are visual objects which in experience are often exactly as vivid and real as if they had external stimuli as causes. These considerations strongly suggest, if they do not rigidly prove, that even in normal vision, the object as experienced depends solely upon higher cerebral processes, beyond the calcarine fissures, and gains its relation to stimuli, retinal images, optic nerve transmission, etc., only because these normally contribute the main forces which mold the higher cortical excitations.

Numerous eminent students of vision, including Helmholtz, have expressed a conviction that in the formation of visual objects, psychical forces are involved which are quite in addition to nervous functions. Because, in retinal rivalry, the two eye images can be represented separately in consciousness it seemed that their fusion under normal conditions could not be due to the physical conjunction of the nerve

currents from corresponding retinal points.[11] The elaborate accuracy with which, as we have seen, this same physical conjunction is actually accomplished in the conduction from the optic chiasma to the calcarine fissures would seem, according to this view, to be calculated only to make it easy for the psychical forces to finish the job. Similar views have been based upon the fact that in binocular vision the brilliance values due to the separate eyes do not summate arithmetically, but rather tend to strike an average.

A more plausible conception, not involving mysterious psychic forces, is that visual objects are determined in their nature by a synthetic cerebral image which lies several stages beyond the calcarine cortex in the onward path of conduction which eventually emerges in some muscular movement. The analysis of visual disorders which are conditioned by diverse cortical injuries, indicates that if such a higher synthetic cerebral image exists, it is the product of a series of operations upon the optic currents, only the first of which is located in the calcarine projection areas. These successive operations correspond to aspects of the visual object which can be distinguished psychologically.

The calcarine area or level, according to Best,[12] is concerned primarily and probably solely with the combination of currents from corresponding retinal points. Such currents are delivered here separately and their point to point synthesis must depend upon special mechanisms provided by the complicated series of nerve elements which exist in the calcarine cortex. The facts of binocular or retinal rivalry indicate that the fusion of corresponding currents takes place less readily the greater the difference in the nature of the currents, and that the further currents resulting from the fusion represent an *average* of the characteristics of the two which are combined, rather than a simple arithmetic sum. Just what the current characteristics are, we can only conjecture, as we have already done in suggesting that stimulation intensity is represented by the basic frequency of the nerve pulses, while two independent forms of modulation of this basic frequency carry the purely chromatic features of the excitation. At any rate, the facts show that the manner of geometrical projection of brilliance and chromatic vision upon the calcarine area is the same for each, although the mechanisms at any point dealing with the two properties are probably separable functionally. The chromatic mechanisms are apparently more easily upset by pathological forces than are those

[11] Helmholtz, H. L. von. Handbuch der physiologischen Optik, 3d ed., *3*, p. 407; 1910.
[12] Best, *loc. cit.*

which represent brilliance or the "light sense" as opposed to the "color sense."

The calcarine apparatus not only combines the impulses from strictly corresponding points, but also those from points which are not too disparate, provided the impulses and their relative distribution in the two eye-fields are sufficiently similar in character. The outcome of this synthesis of disparate features of the two image components must of course be some modification of the currents, passed on to higher centers, which represents the localization of objects in the dimension of depth, or of distance from the eyes. The anatomical connections between the two retinas and the calcarine region are probably fixed by heredity, so that the permanent destruction of any portion of the visual area in this region leaves a sharply defined gap in the visual field which can never be repaired by any process of regrouping or reconnecting between available nerve conductors. The synthesis of corresponding and of disparate binocular currents, on the other hand, is probably dependent upon neural connections which are established by "experience," such connections being limited but not accurately determined by anatomical features. The general law governing such associative combination is seemingly that of the convergence and fusion of sufficiently similar and sufficiently adjacent nerve currents.

The operations carried out by the calcarine mechanisms upon the nerve currents which they receive independently from the two retinas apparently result in modified and simplified currents which are relayed to superordinate cerebral areas for further transformation and transmission. The functions of some of these superordinate areas can be represented most clearly—although inexactly—in psychological terms. At the calcarine level the two halves of the visual field are represented by anatomically and even physiologically separate systems of activity, except that the foveal region has a double representation, but the *visual field* itself, in consciousness, is not split vertically nor has its center a duplex constitution. Unless we are to call upon psychical influences to make up for this lack of correspondence in structure, we must suppose that there are connections beyond the calcarine fissures which bring about the required synthesis physiologically. But this is not all. In consciousness, visual space impressions are combined in a unitary manner with those derived from touch, hearing and other sense departments, so that we localize visual objects not in visual space alone, but in a larger synthetic system. It is most reasonable to suppose that higher center brain activities exist in which this

coördination of diverse sensory data occurs, and that it is upon these higher activities that our consciousness, visual or otherwise, alone directly depends.

These inferences are borne out by the facts of visual brain pathology, which show that disturbances of visual localization can occur in the absence of calcarine injuries, and that the latter, conversely, do not entail any general visual disorientation. The necessity of a mechanism which localizes binocular data in a more general system can be realized when it is considered that voluntary motion of the eyes does not involve a corresponding movement of objects in space as we see it, but rather a displacement of the visual field across the objects, which behave as if fixed in a field larger than the visual but are revealed only where the latter intersects the larger system. Involuntary eye-displacements, however,—as on a moving train or in dizziness (nystagmus)—condition a motion of visual objects in the experience field as a whole. Disturbances of absolute visual localization can exist in which the patient sees objects clearly but is wholly unable to indicate their positions in space, either by pointing or looking. Best believes that the center for absolute visual localization is to be found in the cerebral cortex between the projection areas for vision and touch (and kinaesthesis), but in the neighborhood of the former.

Visual objects, as they appear in the experience of adult observers, cannot be regarded as products of immediate sensory information alone. To a large extent they depend upon past impressions, which combine with and mold the present sensory currents, a process which underlies what the psychologist calls perception, as contrasted with pure sensation. Even stereoscopic localization, or the placing of an object in the dimension of depth, ordinarily involves factors which depend upon memory and association, the so-called secondary criteria of perspective vision. Very imperfect sensory impulses quite commonly result in clear and definite objects in consciousness, as a consequence of a cerebral filling in or completion of the fragments which are actually supplied. These facts show that the visual objects rest at least in part upon brain processes closely allied to memory and imagination, which are almost certainly not operative in the primary projection areas, such as the calcarine. On the other hand, we know that lesions of cerebral regions adjacent to the calcarine, in the so-called visuo-psychic zones, are capable not only of annihilating the power of visual perception but also that of visual imagination and recognition.

The cortical areas for absolute visual localization and certain aspects of vision depending upon retention are seemingly subordinate to even higher levels of integration which are concerned with the intellectualization of visual data, particularly with the processes by which we classify and name objects, or identify them by their names. That such intellectual processes have some influence upon the object itself, considered psychologically as a phenomenon in consciousness, cannot be denied. Practically, they are of the utmost importance, since they involve our ability to reason from and to act upon the basis of what we see. *Visual aphasia* is sometimes known as "psychical blindness," but it is an effect entirely separable from the blindness which results from lesions in the calcarine region, and it is conditioned by injuries to higher association centers.

In the time at my disposal I can thus only imperfectly outline the psychophysiological facts which indicate that the visual objects and their accessories which appear in the normal human consciousness represent the final product of an elaborate series of brain processes, only the first of which is located in the calcarine region. It seems certain that this final or at least *focal* cerebral activity will take the form of a definite neural image, with a distinct pattern derived from that of the calcarine projection images. Between this focal image and the visual object in consciousness, which it directly determines, there is presumably a clear-cut psychophysical correlation, which involves no intermediate physiological or physical links. It is quite impossible, however, to identify the visual object and the focal brain process, since they differ so radically in substance and even in form. We know that the substance of the visual object consists of color surfaces arranged in perspective space, while that of the brain process—in common with all other physical systems—is electrical and is disposed in the space-time manifold of relativity mathematics. That a similarity exists between the two configurations, we also can scarcely doubt, but the formulation of this similarity must involve a very considerable degree of abstraction.[13]

Here we encounter the greatest of the mysteries which exist in an attempt to understand "the optics of the nervous system." Eventually, we shall be able to trace the nerve currents through their

[13] The problem of the pattern relationships of consciousness and the ultimate brain process is being attacked in a courageous manner by the German school of "*Gestalt*" psychologists. See especially: Köhler, W. Die physischen Gestalten in Ruhe und im stationären Zustand, Braunschweig, 1920.

successive transformations, not only from retina to calcarine fissure, but from the latter to the immediate determinant of the visual consciousness; and we shall be able to account for all of these transformations in purely physical terms, as steps in a physically continuous process. But the step from the highest brain image to consciousness is not a transformation; it is a transmutation, accomplished by an alchemy unknown to physics. Here we are led to ask whether we should not add to optics, geometrical, physical, and physiological, a further inquiry: a philosophical optics.

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Mirrors, Prisms and Lenses.—Enlarged and revised edition by James P. C. Southall, Macmillan and Company, New York, 1923.

This is the second edition of what according to the author, is designed to be "a text book which will serve as an introduction to the theory of modern optical instruments." It does not pretend to teach methods of optical design; nor does it present methods for testing the performance of optical instruments. It is purely an elementary theory of geometrical optics of isotropic media—not a treatise on applied geometrical optics.

Accepted as such, we find the book written in excellent style with numerous clean cut illustrative diagrams and some interesting photographs. The mathematical treatment is simple and clear without sacrificing generality. A large amount of valuable information, much of which is embodied in the problems at the end of each chapter, is collected here in a very complete unit.

The impression that the work is almost exclusively geometrical is enhanced by the brief presentation of Huyghens wave fronts, Fermat's law of least time and the relation between the refractive index of a medium and the velocity of propagation of light through that medium.

The fundamentals including the theory of mirrors, prisms and thin spherical lenses are covered in the first eight chapters. Chapter IX deals with thin cylindrical lenses, X and XI with the general theory of centered optical systems, and XII with their practical limitations. In parts of IX, XI and XIII a more than usual amount of space is given to eye glasses and the optics of the human eye, thus reflecting modern progress in this field. Chapter XIV deals with dispersion and the color imperfections of optical instruments and XV with the other inherent imperfections, namely; spherical aberration, the two astigmatic surfaces, coma and distortion. It closes with Seidel's five conditions for their elimination.

The final chapter, XVI, is new with this edition. It is intended to fit into the general scheme of the book only as after-thoughts both interesting and instructive.

C. A. SKINNER

Electrical Vibration Instruments.—By A. E. Kennelly, Professor of Electrical Engineering, Harvard University and The Massachusetts Institute of Technology. Pp. X+450, including over 200 cuts. The MacMillan Co., New York. $6.50.

This book is in part based on researches carried on during the past fourteen years by Professor Kennelly and his co-workers and students at Harvard University and the Massachusetts Institute of Technology. It aims to present the characteristics of such vibration instruments as telephone receivers, oscillographs and vibration galvanometers from the standpoint of "the wonderful and fascinating analogy between the laws of mechanics for a simple vibrational system and the laws of electromagnetics for a simple alternating-current or oscillating-current system" since "an insight into one of these two systems provides a vision for the other."

Partly because of its practical importance, partly because of the possibility of direct methods of treatment, the first fourteen chapters—195 pages—are devoted to the telephone receiver. The theory of mechanical and electrical vibrating systems in general is developed and, in a very thorough discussion, is applied to the receiver. The results of numerous experimental investigations of telephone receivers are given. In Chapters XV to XXI are discussed in turn various types of oscillographs, the theory of their performance and use, and tests thereon. Chapters XXII and XXIII consider vibration galvanometers and the humming telephone.

The more involved parts of the theoretical treatment are covered in 125 pages of appendices. Mention should also be made of the list of symbols used throughout the work, comprising ten pages, and of a bibliography of nearly one hundred titles. While the volume is prepared from the standpoint of the electrical engineer, the physicist will also find much of the material of use for purposes of both instruction and research. This applies particularly to the numerous diagrams showing the behavior of vibratory systems.

F. K. RICHTMYER

ON THE ACTIVE AGENTS IN LUMINESCENT CALCITES, ARAGONITES, AND DOLOMITES

By T. Tanaka

In his study of the cathodo-luminescence of solid solutions of forty-two metals,[1] the author determined the location of the luminescence bands characteristic of those metals, the frequency intervals of each one, and certain regular relations existing between these frequency intervals and the atomic weight.

These results give a principle by which the identity of a metal to which certain bands are known to be due can be ascertained, and by using this principle the author has investigated some luminescent substances the active agents of which have long been subjects of discussion. In the present paper the cathodo-luminescence of certain calcites and related minerals will be considered. Most of these were furnished by the department of mineralogy of Cornell University, through the kindness of Professor Gill, to whom the author is especially indebted.

The study of the luminescence of calcites has a long history. It can be traced back to the work of Becquerel, beginning in 1859.[2] In his later experiments Becquerel[3] found that the luminescent samples of calcite contained a fair quantity of manganese (up to 2.7%) while less brilliant samples contained manganese in very small proportions, or not at all, so far as ordinary chemical methods could determine. He[4] also mentions that, to produce luminescence in a marked degree, a few per cent of salts of some alkaline metals as sodium, lithium, or rubidium must be present. This action of alkaline metals may be analogous to that of fluxes in Lenard and Klatt's sulphides.

More recently, Headen[5] made precise chemical analyses of several samples of calcite. He found in each sample a few hundredths per cent of the rare earth metals, and noticed that, in strongly luminescent calcites, the ratio of yttrium oxides to cerium oxides was a few times greater than in samples of feebly- or non-luminescent calcites. Hence he was inclined to attribute the effect to salts of the yttrium group.

[1] Tanaka: J. O. S. A. & R. S. I., *8*, p. 289; 1924.
[2] Becquerel, E.: Ann. de Chimie et de Physique, (3), *57*, p. 40; 1859.
[3] Becquerel, E.: Comptes Rendus, *103*, p. 1098; 1886.
[4] Becquerel, E.: Comptes Rendus, *107*, p. 892-895; 1889.
[5] Headen, W. T.: Am. Jour. of Science, (4), *21*, p. 301-306; 1906.

But it seems unlikely to the present author that so small a change in the concentration of the active agent should produce an essential change in the luminescence. Such a result is inconsistent with facts previously discovered experimentally. For example, according to Bruninghaus's experiment[6] the increase of MnO dissolved in CaO from 0.01% to 0.10% changes the intensity of cathodo-luminescence only from 7 to 9.

Quite recently, Nichols, Howes and Wilber[7] studied the cathodo-luminescence of calcites, some of which were the same samples that are here studied in further detail. In conformance with Becquerel's opinion, they attributed the luminescence of calcites to traces of manganese salts present in them. This investigation may be regarded as a continuation of their researches.

In the case of each sample, the positions of the luminescence bands present were determined by repeated experiments. Each band thus located was then found to be, within the limits of error in measurements, identical with some band of one of the metals whose characteristic luminescence bands had been previously determined.[8]

In the following tables the wave-lengths of the crests in the spectrum of the sample studied are given in A.U. Where the readings do not coincide with those for the corresponding metal crest as determined in the investigation just cited the discrepancy is indicated: e.g. 5795(4) which means that while the reading for the calcite crest was 5795, that of the crest with which it is identified was given as 5794.

TABLE 1. *Calcites*

Substance	Active Agents	Bands identified.
Calcite I	Mn(12)	5910, 5893(6), 5831, 5795(4), 5754, 5690(1), 5617(8), 5573(4), 5524(5), 5469(0), 5423, 5367(5).
	Dy(3)	5872(3), 5719(0), 5659(61).
Calcite II	Mn(7)	5855, 5896, 6794, 5523(5), 5489(8), 5432, 5423.
	Yt(6)	6133(5), 5817, 5762(3), 5669(0), 5599, 5531.
	Tl(3)	6075(3), 6010, 5710(1).
Calcite III	Mn(9)	5897(6), 5855, 5831, 5793(4), 5742(1), 5681(2), 5632(1), 5558(9), 5524(5).
	Dy(4)	5871(3), 5781(0), 5720, 5603.

[6] Bruninghaus, M. L.: Comptes Rendus, *144*, p. 839; 1907.
[7] Nichols, Howes and Wilber: Physical Review, (2), *12*, p. 351; 1918.
[8] Tanaka: J. O. S. A. & R. S. I., *8*, p. 289; 1924.

TABLE 1. *Continued*

Substance	Active Agents	Bands identified
Calcite IV	Mn(10)	6161(58), 6127(31), 5896, 5853(5), 5834(1), 5794, 5755(4), 5740(1), 5681(2), 5618.
	Yt(6)	6053, 6017(6), 5972, 5929, 5820(17), 5670,
	Dy(4)	5938(6), 5875(3), 5781(0), 5718(20).
Calcite V	Mn(11)	6202(3), 6157(8), 6130(1), 5977, 5910, 5893(6), 5830(1), 5794, 5741, 5689(1), 5616(8).
	Yt(4)	6104(5), 6053, 5929, 5669(0).
	Tl(3)	5948, 5771(69), 5710(1).
	Dy(1)	5873.
Calcite VI	Mn(12)	6031, 5977, 5973(4), 5910, 5830(1), 5795(4), 5755(4), 5739(41), 5692(1), 5680(2), 5631, 5559.
	Yb?(7)	5962(4), 5865(6), 5776, 5717(6), 5598(9), 5577, 5522.
Calcite VII	Mn(13)	6427, 6291(3), 6225(7), 6202(3), 6158, 6128(31), 6099(8), 5894(6), 5953(5), 5753(4), 5740(1), 5691, 5631.
	Dy(5)	6383(5), 6272(5), 6069(8), 5809(11), 5659(61).
	Sa(3)	6041, 6019(7), 5966.
Calcite VIII	Mn(9)	6426(7), 6361, 6286(9), 6129(31), 6044(6), 5981(77), 5898(6), 5853(3), 5683(2).
	Yt(3)	6491, 6199(7), 5743(2).
Calcite IX	Mn(15)	6544, 6502, 6462(4), 6427, 6360(1), 6288(9), 6204(3), 6132, 6095(8), 5979(7), 5852(5), 5793(4), 5753(4), 5690(1), 5631.
	Yt(2)	6053, 5928(9).
Calcite X	Mn(19)	6545(4), 6464, 6426(7), 6360(1), 6225(7), 6201(3), 6159(8), 6129(31), 6099(8), 6048(6), 5980(77), 5973(4), 5909(10), 5794, 5752(4), 5680(2), 5630(1), 5575(4), 5523(5).
	Dy(2)	6275, 5844(2).
Calcite XI	Mn(13)	6503(2), 6427, 6292(3), 6228(7), 6159(8), 6097(8), 6047(6), 5977, 5896, 5854(5), 5755(4), 5693(1), 5631.
	Dy(5)	6422, 6348, 6001, 5934(6), 5809(11).
Calcite XII	Mn(10)	6359(61), 6202(3), 6157(8), 6098, 5977, 5910, 5795(4), 5741, 5580(2), 5621(18).
	Sa(6)	6533(4), 6444(6), 6269, 6120(18), 6039(41), 5841.

NOTES ON TABLE 1.

CALCITE I. (From Crugers, Westchester County, New York). Luminescence orange of medium intensity. Twelve manganese and three dysprosium bands were recognized.

Dysprosium is a rare earth metal belonging to the yttrium group. It is well known that yttrium is of very frequent occurrence in calcium minerals, and that it is almost always associated with traces of other members of its group. Furthermore, it was found by the author in the studies previously described, that, in calcium carbonate as solvent, dysprosium is one of the active agents producing the greatest luminescence, the color being orange. Therefore the participation of dysprosium in the luminescence of this sample of calcite is quite probable; while it would be difficult to explain such a luminescence spectrum by the occurrence of yttrium, samarium, thallium, cerium, or some other metal.

It need hardly be said that almost all samples of calcite contain manganese salts, and that manganese dissolved in calcium carbonate is a very prominent active agent. Other probable impurities of calcite, discoverable by ordinary chemical analysis, are iron, magnesium and zinc, but these are by no means prominent active agents, as may be seen by referring to the paper already cited. The luminescence of this calcite however should doubtless be attributed chiefly to manganese, especially as the presence of a small quantity of that metal in the sample was also proved by Volhard's reaction.

CALCITE II. (From Mahopac Mines, Putnam County, New York.). Luminescence orange but quite faint. Seven manganese, six yttrium, and three thallium bands were recognized.

Since the manganese bands are abundant in the region of smaller brightness, the chief effect is to be attributed both to yttrium and to manganese, while thallium plays some part. The wide distribution of yttrium and thallium is generally recognized, so that their occurrence in the calcite is not surprising. By Volhard's reaction only faint traces of manganese could be detected.

CALCITE III. (From Tompkins Cove, Westchester County, New York.) It showed a luminescence of medium intensity, and a sharp spectrum curve with well-defined subordinate crests was obtained. Nine manganese and four dysprosium bands were recognized. The probability of the occurrence of dysprosium has already been discussed in the case of Calcite I. By Volhard's reaction the presence of a fair quantity of manganese in the present sample was detected; hence the chief effect in this case is doubtless due to that metal.

CALCITE IV. (From the Tungsten Mine, Long Hill, Connecticut.) It showed a somewhat faint luminescence, and a spectrum curve with a rather broad summit was obtained. Ten manganese, six yttrium, and four dysprosium bands were found. The chief effect is to be attributed to manganese and yttrium, while dysprosium plays a less important part.

By Volhard's reaction the presence of a comparatively large quantity of manganese was detected in this sample, yet the luminescence was rather faint in comparison with that of other samples containing less manganese. It is not reasonable to attribute this fact to a too great concentration of manganese; because according to the researches of Bruninghaus,[9] in order to destroy the luminescence of a mixture of calcium carbonate with a manganese salt the manganese must increase to ten per cent or more. The faintness may be due to (1) the absence of alkaline metals whose presence would be favorable to the phenomenon, (2) the presence of some other metal or metals, whose presence is unfavorable to it, or (3) failure to have received some natural treatment which, perhaps, the substance must undergo in order to show high luminescent power. The presence of yttrium in samples of fluorspar from the same locality was reported by Humphreys.[10]

CALCITE V. (From Mahopac Mines, Putnam County, New York.) This sample was from the same locality as Calcite II. Nevertheless, it showed a fairly bright luminescence. Eleven manganese, four yttrium, three thallium bands were found; also one dysprosium band.

It may not seem safe to assert the occurrence of dysprosium from the presence of one band only; however, a sharp band with its crest at 6001 (the location of the crest of one of the dysprosium bands given in Table 56 of the previous paper already cited) appeared at one time while working with this calcite. This band was eliminated from the table for Calcite V, because it did not occur steadily; but its appearance may serve to confirm the supposition that dysprosium is present.

Volhard's reaction proved the presence of a fair quantity of manganese, probably the chief active agent in this sample. The active agents are the same as those in Calcite II, which is natural, as the two came from the same locality. The difference in the intensity of the luminescent light is due to the difference in the quantities of manganese contained in them.

[9] Bruninghaus, M. L.: Comptes Rendus, *144*, p. 839; 1907.

[10] Humphreys, W. J.: Astrophysical Journal, *20*, pp. 266-273; 1904.

CALCITE VI. (From Bear Mountain, Rockland County, New York). Luminescence of medium intensity. Twelve bands due to manganese were found, with seven due to an unknown element, which must be the same as that found in the study of the zinc sulphides to be described in a forthcoming paper. This was supposed to be ytterbium, a rare-earth metal of such wide distribution that its occurrence in this sample would not be surprising. The presence of a fair quantity of manganese in the sample was detected by Volhard's reaction.

CALCITE VII. (From Cumberland, England). Luminescence a fairly bright reddish orange. Thirteen manganese, five dysprosium, and three samarium bands were found. The presence of a small quantity of manganese was also proved by Volhard's reaction. Humphreys has shown that many samples of fluorspar from the same locality contain fair quantities of yttrium, but careful studies of the spectrum curve in this case failed to disclose a single band due to that element.

CALCITE VIII. (From Colorado). Luminescence a rather faint orange; spectrum curve beautifully jagged. Nine manganese and three yttrium bands were detected. This sample and the next were furnished by Professor W. P. Headen. He mentions them in his paper[11] as "yellow, strongly phosphorescent calcites" and proved by a careful chemical analysis the presence of comparatively large quantities of yttrium. But while some yttrium bands appear, yttrium certainly cannot be the chief active agent of the luminescence. The presence of a small quantity of manganese was detected by Volhard's reaction.

CALCITE IX. This sample came from the same locality as Calcite VIII, and showed a similar, though somewhat brighter, luminescence. Fifteen manganese and two yttrium bands were found. The result is in every way similar to that of Calcite VIII. The presence of manganese was detected by Volhard's reaction.

CALCITE X. (From Franklin Furnace, New Jersey). Luminescence very bright, reddish orange; spectrum curve jagged. Nineteen manganese and two dysprosium bands were found. The presence of a fair quantity of manganese was detected by Volhard's reaction.

CALCITE XI. (From Lowville, New York). Luminescence very bright. Spectrum curve quite similar to that of Calcite X. Thirteen manganese and five dysprosium bands were found. The presence of a fair quantity of manganese could be detected by Volhard's reaction.

CALCITE XII. This sample was taken out of an old Crookes tube. It showed a reddish orange luminescence of medium intensity. Ten manganese and six samarium bands were found. The presence of manganese could be detected by Volhard's reaction. The occurrence of samarium may be regarded as probable since samarium, which shows a prominent luminescence in the orange region similar to that of manganese, is a widely distributed element.

CALCITE XIII. The origin of this and of the remaining six samples of calcites is unknown. In this case twelve manganese and three thallium bands were identified, in the region 6300-5600. The intensity of luminescence was rather faint. The presence of traces of manganese was shown by Volhard's reaction.

CALCITE XIV. Fourteen manganese and five dysprosium bands were identified, in the region 6500-5500. The luminescence was very bright. The presence of manganese was shown by Volhard's reaction.

CALCITE XV. The luminescence was so faint that the author found it necessary to accustom his eye to darkness for about fifteen minutes before he could make any measurements. Eleven bands of strontium and two of cerium were identified in the region 5265-5125. The luminescent color was greenish white, differing from that of the other calcites studied. No manganese could be detected by Volhard's reaction.

CALCITE XVI. Nine manganese and three dysprosium bands were found, in the region 6360-5690. The presence of manganese could be detected by Volhard's reaction.

[11] Headen, W. P.: American Journal Science, 4, *21*, pp. 301-306; 1906.

CALCITE XVII. Nine manganese and three yttrium bands were identified, in the region 6500-5500.

CALCITE XVIII. Twenty manganese bands were found, in the region 6675-5450. No bands due to other metals appeared.

CALCITE XIX. Fifteen manganese and four yttrium bands were identified, in the region 6600-5450.

TABLE 2. *Limestones, Aragonites, etc.*

Substance	Active Agents	Bands recognized
Crystalline Limestone I	Dy(11)	6100(1), 6001, 5907(5), 5873, 5810(1), 5780, 5749(50), 5720, 5690(1), 5660(1), 5632.
	Mn(7)	6048(6), 5978(7), 5895(6), 5855, 5752(4), 5559, 5430(2).
Red Band	Tl(4)	5951(48), 5884(7), 5711, 5602(0).
Blue Band	Dy(7)	4970, 4944(7); 4925, 4900(3), 4885(2), 4838(9), 4798(6),
	Mn(2)	5005, 4885(3).
Crystalline Limestone II	Mn(8)	5896, 5858(5), 5834(1), 5794, 5740(1), 5693(1), 5631, 5616(8).
	Dy(6)	5998(01), 5811, 5779(0), 5722(0), 5661, 5603.
	Tl(2)	5947(8), 5657(5).
Old Lime	Mn(12)	6361, 6288(9), 6228(7), 6158, 6099(8), 6048(6), 5974, 5911(0), 5752(4), 5691, 5628(1), 5574.
	Dy(2)	5845(2), 5812(1).
Aragonite I	Mn(17)	6227, 6157(8), 6100(98), 6029(931), 5974, 5910, 5893(6), 5857(5), 5831, 5794, 5754, 5741, 5682, 5632(1), 5560(59), 5470, 5423.
	Sr(3)	5961(59), 5818(6), 5504(6).
Aragonite II	Sr(32)	5771(0), 5718(9), 5680, 5636, 5610, 5576(5), 5550, 5540, 5509(8), 5472, 5440(39), 5406, 5386(5), 5374(3), 5347(6), 5340(1), 5308(7), 5265(8), 5245(6), 5230(1), 5193, 5186(5), 5154(5), 5125, 5096, 5084, 5050(49), 5039(8), 5014, 5009(10), 4980, 4954.
	Cu(2)	5485, 5435.
Dolomite I	Dy(15)	6001, 5933(6), 5873, 5750, 5662(1), 5634(2), 5601(3), 5547, 5518(9), 5410, 5383(4), 5332, 5305(6), 5255, 5205.
	Mn(9)	5971(4), 5894(6), 5829(31), 5792(4), 5682, 5572(4), 5487(8), 5469(0), 5421(3).
Dolomite II	Mn(16)	6542(4), 6462(4), 6369, 6293, 6227, 6160(58), 6100(98), 5973(4), 5894(6), 5831, 5796(4), 5739(1), 5682, 5628(1), 5574, 5523(5).
	Yt(1)	6054(3).
Magnesite	Mn(10)	6543(4), 6461(4), 6290(3), 6206(3), 6131, 6046, 5979(7), 5910, 5855, 5794.
	Dy(3)	6384(5), 6068, 5842.

NOTES ON TABLE 2.

CRYSTALLINE LIMESTONE I. (From Amawalk, Westchester County, New York.) Luminescence of medium intensity. Eleven dysprosium, seven manganese, and four thallium bands were identified.

Only a trace of manganese was shown by Volhard's reaction, though the manganese bands appearing in the spectrum were quite bright. The failure of Volhard's test may not mean a real scantiness of manganese, since the presence of chloride prevents the formation of permanganic acid, upon which this method of detection depends.

A fair amount of dysprosium seems to have been present, since in the case of this sample dysprosium plays a more important part in the presence of the faint blue band whose components are given in the second part of the table for this sample. The occurrence of a blue band similar to this was very clearly recognized in the author's experiment upon a solid solution of dysprosium in calcium carbonate.

CRYSTALLINE LIMESTONE II. (From Verplanck's Point, Westchester County, New York.) Luminescence rather faint. Eight manganese, six dysprosium, and two thallium bands were identified. The presence of a fair amount of manganese was detected by Volhard's reaction.

OLD LIME. This sample was from cylinders originally prepared for a lime light. When first tried it was almost inactive, but after being heated to a red glow for about thirty minutes it became highly luminescent. The envelope of its spectrum curve had its maximum at about 5950 A.U. Twelve manganese and two dysprosium bands were recognized. The presence of a small quantity of manganese was detected by Volhard's reaction.

ARGONITE I. This sample consisted of fine powder taken out of an old Crookes tube, and showed a brilliant orange luminescence, very similar to that of Calcite XII. Seventeen manganese and three strontium bands were identified. The presence of a small quantity of manganese was detected by Volhard's reaction.

ARGONITE II. This sample came from Arizona. It showed a beautiful green luminescence in the early stages of the cathode ray bombardment, but after about ten minutes this turned to a faint whitish color. The appearance was entirely different from that of the previous sample. Thirty-two strontium and two copper bands were found.

The frequent occurrence of traces of strontium in aragonites has been known for a long time. Indeed, for many years previous to the date of the discovery of the law of dimorphism, the difference between the crystalline forms of calcite, and aragonite, was believed to be due to the presence of strontium salts in the aragonite. Becquerel[12] described aragonite as a mineral showing a greenish blue luminescence, which did not change its color when the mineral was transformed into calcite by being heated. He attributed the difference of the luminescent colors of aragonite and calcite to the presence of strontium in the aragonite. But later[13] he seems to have believed it possible that the crystalline form altered the luminescence, since every sample of aragonite studied by him showed a green instead of an orange color. The present result confirms his earlier opinion.

The presence of copper in this sample was confirmed by ordinary chemical analysis, and the blue tint of its natural color is believed to be due to the presence of this metal. But the copper does not play any great part in the luminescence. Volhard's reaction did not detect the presence of any manganese.

DOLOMITE I. (From the Tilly Foster Mine, Putnam County, New York.) Luminescence, orange, rather faint. Fifteen dysprosium and nine manganese bands were recognized.

This case was an exception, in that dysprosium was a more important agent of luminescence than was manganese. By Volhard's reaction the presence of a fair amount of manganese was detected. In all five cases, in which manganese did not show a prominent lumines-

[12] Becquerel, E.: La Lumiere, *1*, p. 354; 1867.

[13] Becquerel, E.: Comptes Rendus, *53*, p. 23; 1886.

cent power in comparison with other agents, namely in Calcite II, Calcite IV, Calcite XV, Crystalline limestone I, and this sample of dolomite, the luminescence was quite faint.

DOLOMITE II. (From Neusinshan, Manchuria, China.) Luminescence of medium intensity, the spectrum curve forming a broad summit. This seems to be a characteristic of dolomites. Sixteen manganese bands and one yttrium band were found. Of course the presence of yttrium in such a case is subject to doubt. A small quantity of manganese was detected by Volhard's reaction.

The probable impurities of dolomites, as determined by ordinary chemical analyses, are the same as those of calcites, so that no additional discussion will be necessary here.

MAGNESITE. (From Neusinshan, Manchuria, China.) Luminescence red and of medium intensity. The envelope of its spectrum curve showed a well-defined maximum at about 6450. Ten manganese and three dysprosium bands were identified. The presence of a small quantity of manganese was detected by Volhard's reaction.

SUMMARY

(1) The chief active agent in the luminescence of calcites, crystalline limestones, and dolomites is in most cases manganese; and their luminescent color is orange or reddish orange.

(2) Sometimes manganese does not show a prominent luminescent power; and in such cases the luminescence is generally faint.

(3) Sometimes strontium acts as the chief active agent, giving a greenish, comparatively faint luminescence; such cases occur frequently in aragonites.

(4) Other active agents are dysprosium, yttrium, thallium, and samarium.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
JUNE, 1923.

CERTAIN EFFECTS PRODUCED BY CHILLING GLASS*

By A. Q. Tool and C. G. Eichlin

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ABSTRACT

Data are secured from the heating curves for chilled and annealed glasses which appear to show. (1) That cooling glass slowly through the annealing range allows some molecular readjustment which may include the formation of large molecules or aggregates, while cooling it rapidly prevents such readjustments, (2) That these readjustments appear to change such characteristics of the glass as its density, refractive index, homogeneity, stability, etc., and (3) That heating glass for long periods at a given temperature allows the glass to come to a condition of equilibrium which, over a wide range, varies with the treating temperature.

The data on which these conclusions are based are obtained by a method of curve analysis used to compare changes in the form of the heating curves caused by different heat treatments of the glass.

I. Introduction

In previous articles[1] certain phases of the endothermic effect observed in glass while it is being heated have been fully discussed. In these articles it was shown that as a glass under steady heating conditions enters a definite temperature range, a marked decrease in its heating

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[1] B. S. Scientific Paper No. 358; 1920.
J. Optical Soc. Am., *4*, p. 340; 1920.

rate begins, although the heating rate of its surroundings remains constant. Since the rate at which heat is supplied to the glass under these conditions naturally remains either constant or increases, this retardation in the heating rate of a glass indicates that within or near the temperature range where the effect is observed some change or transformation takes place causing a heat absorption which is abnormal relative to the uniform absorption at both lower and higher temperatures. The temperature range within which this abnormal absorption occurs is slightly above those temperatures usually employed in annealing the glass. After this critical range is passed, the glass, particularly if from a well annealed sample, shows a tendency for a time to heat at a faster rate than its surroundings. Finally, however, approximately steady heating conditions are re-established.

It was shown also, particularly in two papers[2] presented before the Optical Society, that effects of this character observed in chilled glass are quite different from those in annealed glass. With chilled glass the decrease in the heating rate in the critical range and the maximum temperature difference between the glass and its surroundings are smaller than for the same glass when well annealed. This indicates that the quantity of heat absorbed by an annealed glass on being heated through the critical range is greater than that absorbed by a chilled glass of the same type. After the critical range has been passed, there is also a smaller tendency for the chilled glass to accelerate its rate of heating. Furthermore, there is often evidence of the existence of an exothermic effect in chilled glass which precedes (and perhaps extends into) that region in which the endothermic effect is normally observed.

These characteristic differences between annealed and chilled glasses become more marked as the severity of the chilling is increased, that is, as the rapidity of the previous cooling through the critical temperature range is increased or as the temperature from which a given type of cooling begins is raised. In addition, as this investigation shows, these differences are modified by the length of time the glass is held at those temperatures from which the chilling begins.

In these earlier investigations and also in the experiments preliminary to this investigation data were obtained which indicate that glass tends to assume a condition dependent on the annealing temperature, the time of annealing, and the mode of cooling. In fact, it appears that

[2] "Further Results on the Heat Absorption of Glass," Dec. 27-29, 1920.
"Some Thermal Effects Observed in Chilled Glass," Oct. 24-26, 1921.

glass, when it is held for a sufficient time at a given temperature, will assume a state of equilibrium peculiar to that temperature. It appears also that this equilibrium condition may be preserved to a greater or less degree by sudden chilling; while complete annealing treatments including slow cooling may often produce a condition which does not correspond (insofar at least as the heat effects just discussed are concerned) to the annealing temperature but to some other, usually a lower one. This latter temperature, for want of a better term, will be called the "effective" annealing temperature.

These changes in the character of the glass with temperature and treatment demand a further study of the variations or modifications in the heat effects. The importance of investigating any changes in glass resulting from different procedures in its annealing and the value of determining whether glass actually assumes a state of equilibrium corresponding to an "effective" annealing temperature determined by the type of glass and its treatment, becomes more evident when it is considered that the various possible conditions the glass may assume undoubtedly entail differences in its density, refractive index, durability, stability, etc. This investigation, a continuation of the previous studies, was undertaken chiefly for the ultimate purpose of gaining such information as the exothermic and endothermic effects might yield concerning the character and properties of glass, although the immediate purpose was to devise a comparative method which would serve to make clear the interpretations of the results discussed in the previous paragraphs.

II. METHOD AND APPARATUS

1. THE GLASS AND ITS PREPARATION

Data were obtained for several glasses, but in the most extended series of experiments a borosilicate crown (B. S. Melt 431)[3] was used. Since the results from this series appeared in most respects representative, the data presented here were obtained principally from this type of glass. The glass was chosen from large, striae-free fragments broken directly from the pot, which, as a result of the slow cooling of

[3] The composition of this glass which was made by the Optical Glass Section of this Bureau was kindly furnished by that section. These values are the averages of two analyses.

Borosilicate Crown, Melt B. S. 431

SiO_2	64.52	K_2O	10.84
R_2O_3	0.35	Na_2O	7.85
ZnO	2.66	B_2O_3	11.93
BaO	2.56		

this large mass, were found to be fairly well annealed. These fragments were then broken into small pieces and sorted by sifting so that the particles used in the tests varied in diameter from about 0.5 to 2.1 mm. An estimate of their average weight based on actual weighing of samples containing a large known number was 2.5 mg.

In the chilling treatment a six-gram lot of this cracked glass was placed in a thin platinum crucible and suspended in a furnace held at the temperature from which the chilling was to begin. The total time allowed for the glass to reach this temperature and to adjust itself varied from 15 minutes to 2 hours or more. In obtaining the data for Table 1, for example, the glass after fifteen minutes—the minimum time in which it was deemed possible for it not only to have reached the desired temperature, but also to have been allowed some time for possible readjustment—was removed quickly from the furnace and plunged into water. In this operation it appeared that the temperature of the glass fell from that of the furnace to one below boiling water in less than three seconds. When the chilling was done in air the glass was removed from the furnace and scattered quickly over a large area on a glass plate.

The effects on a glass chilled in water appeared greater than those for one chilled in other materials, but were somewhat less uniform than those obtained by chilling in air. The greater effects observed through the use of water were attributed to the relatively good contact between it and the glass and also to its great latent heat. The other chilling agents tried, liquid air, mercury, oil, etc., produced effects which beyond slight variations in magnitude were different in no other respect from those obtained by chilling in water; and since their use is obviously more difficult, they were not extensively employed.

The temperature of the furnace used for heating the glass before chilling could be held constant for long periods of time and was uniform throughout a much larger volume than that occupied by the crucible. The temperature of the glass just before its removal from the furnace will be referred to as the "chilling" temperature. It was assumed to be that determined by a thermocouple whose junction was practically in contact with the crucible. This assumption was justified because tests with an auxiliary thermocouple whose junction was placed in the center of the mass of glass indicated that after 14 minutes the glass at the center had reached and then maintained a temperature within one degree of the temperature indicated by the thermocouple in contact with the outside of the crucible.

As shown in Table 1, the chilling temperatures were chosen at frequent intervals, particularly throughout the critical range (550° to 580°C) for the original glass. The data given for each chilling temperature are based on results obtained on at least two lots of glass chilled at different times. As no marked variations in the results for these different lots were observed, it was concluded that the chilling temperatures were determined with reasonable consistency.

2. DETECTION OF EXOTHERMIC AND ENDOTHERMIC EFFECTS

(a) Apparatus.

For the detection of the thermal effects the apparatus which has been described fully in previous publications,[4] was that usually required when a differential thermocouple is used in the investigation of similar effects in other materials. The glass sample containing one junction of a Pt.Rh.-Pt.-Pt.Rh. differential thermocouple was packed in close contact with a neutral body containing the other junction, and placed in a furnace whose rate of heating could be easily controlled. The deflections of a high-sensitivity galvanometer in series with the differential thermocouple served to detect differences in temperature between the glass and the neutral body. Between 200° and 600°C a difference of one degree between the junctions produced a deflection of about 2.3 cm. These deflections were read every minute or oftener, while the glass was being heated.

A Pt.-Pt.Rh. thermocouple, formed by a third wire of platinum leading to one of the junctions of the differential thermocouple and one of the Pt.Rh. wires, served to determine the temperature of either the glass or the neutral body. During the heating these temperatures were determined at ten-minute intervals by means of a potentiometer. The rate of heating was such that the temperature of the glass increased about 60°C in each interval. The constancy of this rate after reaching 200°C was such that it seldom deviated from the mean value per minute by more than 3% in a single experiment or by more than 0.5°C from a value of 6°C per minute for the whole series.

(b) Packing.

In the method of packing one change was made in that previously described. This consisted in replacing the small inner porcelain tube within which the glass and the neutral body were packed with one of platinum. This aided the enclosing silver tube somewhat in equalizing the temperature inequalities of the furnace walls, and brought an

[4] *Loc. cit.*

isothermal surface nearer the glass. As the glass appeared to be a slightly better conductor of heat than the neutral body (120 mesh alundum), it was usually at a somewhat higher temperature while they were being heated. The difference in temperature between the two junctions, which were 2 cm apart was, however, seldom more than 3°C. During the heating this temperature difference for annealed glasses was constant or changed only slightly throughout the whole range preceding the endothermic effect. This uniformity existed also for chilled glasses until the temperature was reached where the exothermic effect became evident.

Variations in the observed differences in temperature between the glass and the neutral body either in the same test or between different tests depended on several factors, among which were the magnitude and the constancy of the heating rate, the thermal characteristics and relative insulation of the glass and neutral body, the positions of the junctions of the thermocouples, and possible slight differences in the thermoelectric properties of these junctions.

Perfect duplication of all conditions being impossible, even when the packing was done with considerable care and the rate of heating closely controlled, it was considered advisable to establish first the reliability of the method of curve analysis described below. For this purpose repeated tests were performed on specimens of glass obtained for each chilling temperature, an additional precaution being that no two of the tests on a glass receiving the same treatment were performed consecutively.

3. ANALYSIS OF THE CURVES

The curves for showing the differences in temperature between the glass and the neutral body during heating were obtained by plotting the galvanometer deflections, or the actual differences in temperature represented by them, as ordinates, and the corresponding temperatures of the glass as abscissae, these temperatures being interpolated from the temperatures determined at the ten-minute intervals. In the case of the original unchilled glass the curve is a straight line (see Fig. 1) from a temperature of about 150°C until the critical range is neared. Where this range begins (at a temperature of about 550°C) the curve drops rapidly, showing a marked retardation in the heating rate of the glass. It continues to drop until about 580°C, where it returns sharply to a new level lower than the previous one, and then follows another straight line. This new line is followed until those temperatures are

reached where the glass softens sufficiently to allow the particles under the heating conditions to fuse or sinter slightly. Variations depending on the heating rate, the manner of packing and the condition and character of the glass then arise.

The fact that the level which the curve assumes after the critical range has been passed is lower than that previous to it probably indicates that the glass has acquired either a lower heat conductivity, a higher specific heat or possibly both. An improbable explanation which might seem to account for this effect is that a slight fusion or spheroiding of the particles may occur at these temperatures, causing the glass to shrink from the walls of the packing thus hindering the flow of heat to the glass. Offsetting such a shrinkage, however, there is a marked increase in the thermal expansivity in this temperature range as has been shown by Peters and Cragoe.[5] Furthermore, the tendency to fuse at the temperature attained in these experiments was very small, since the heating was stopped at temperatures which permitted the easy removal of the thermocouple from the glass. Besides, this change in level persists and is independent of the condition of the glass, whether powdered, in particles, or in one large piece. These facts make it evident that this difference in level cannot be satisfactorily explained by a possible shrinkage of the glass.

With the chilled glass (See Fig. 1) the difference in level between the parts of the curve preceding and following the critical range is still apparent; certain variations in form, however, become quite evident. Thus, for the more severely chilled specimens the curve at temperatures just below the critical range rises to a maximum, due apparently to an exothermic effect as mentioned in the introduction.[6] Also as stated there even in the moderately chilled glasses (See Fig. 2) the drop of the curve from the first level to a minimum, and the return from this minimum to the second level are markedly less than for annealed glass.

A graphical method for analyzing and comparing these differences between the curves for chilled and annealed glasses, and for locating the approximate temperatures at which the critical range begins and ends will now be described, and illustrated in Fig. 1. In this method lines coinciding with the slopes of the curve in the two levels described

[5] Jour. Optical Soc. Am., *4*, p. 105; 1920.

[6] It is also possible that the height and slope of that first portion of the curve, which seems level, is affected somewhat by this effect, even before the rise becomes apparent, but it appears that the magnitude of such a modification, even if existent, is too small to be considered here.

are drawn as shown. Then two other lines are drawn coinciding with the slopes where the drop from the first level and the return to the second are steepest. These lines intersect at points A, B and C. The temper-

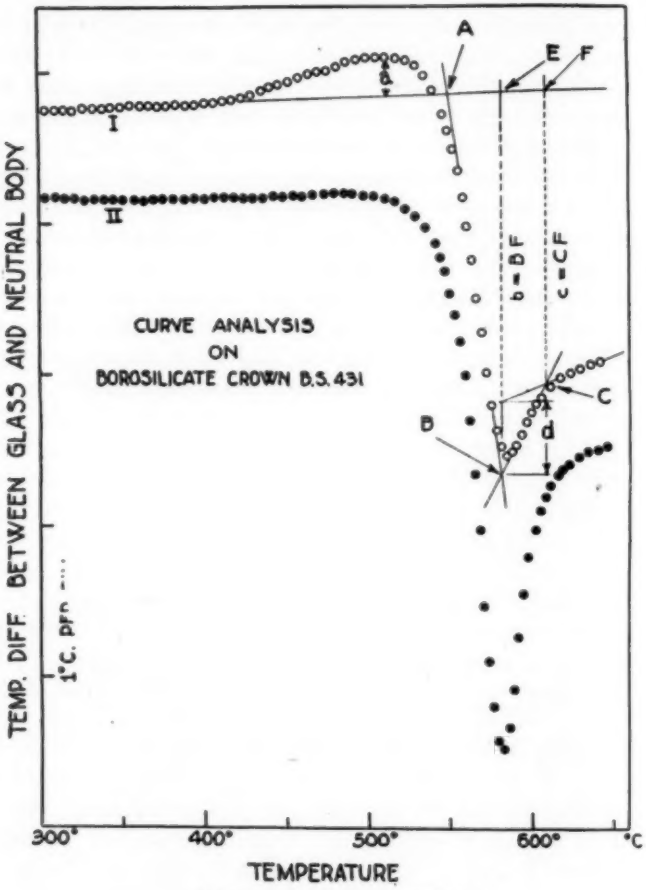

FIG. 1. *Method of curve analysis.*
I. *Held for 15 minutes at 565°C, chilled in water.*
II. *Original, untreated.*

atures corresponding to A and B are convenient points, which for a given rate of heating may be used to specify the limits[7] of the critical

[7] It was shown in a previous paper (l.c.) that the points A and B shift towards higher temperatures when the rate of heating is materially increased. Because of the constancy of

range for the endothermic effect. This method of analysis was used to determine the temperatures given in Table 1, which also shows data obtained by this method for the other characteristics of the curves. These are the differences in temperature corresponding to: the rise, *a*, the distances, *b* and *c*, of the points *B* and *C*, respectively, below the line representing the initial slope; and to the distance, *d*, of the point *B* below the line representing the final slope. While this method of analysis can at best be only qualitative it gives an excellent means of comparing the forms of the curves and showing the changes in them as the chilling temperature and other factors in the treatment of the glass are varied.

III. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

1. CHANGES IN FORM OF HEATING CURVES

(a) By varying the chilling temperature.

To visualize the progressive changes in form which occur in heating curves of the type just discussed and shown in Fig. 1, as the chilling temperature is increased, a series of curves has been arranged by placing them arbitrarily one above the other, as shown in Fig. 2. The glass used in procuring the latter curves was obtained from a series of samples, each of which after the 15 minutes allowed for heating and adjusting had been chilled in air from one of the chilling temperatures, 525°, 550°C, etc., as indicated. They are so drawn that all points representing the observations, which were taken at approximately 3° and 6° intervals, lie within the width of the line.

Comparing the curve obtained for the chilling temperature 525°C with the curve obtained for the original glass, shown in Fig. 1, it will be seen that chilling from this temperature produces no noticeable change in the form of the curve. Even on chilling from 550° very little change of any sort is apparent, beyond a slight shortening of *b*, the drop from the first level to the minimum; and of *d*, the return from the minimum to the second level. In chilling from 575°, however, the changes become very marked, the rise, *a*, from the original level now being quite evident, while the decrease in both *b* and *d* is much greater. Chilling from 600° causes these changes to become even more pronounced; but chilling from a still higher temperature produces very little further modification, as can be seen from the two upper curves.

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the rate of heating used in this investigation, however, any deviations observed in these temperatures cannot be ascribed to a change in rate.

In fact, results have been obtained which show that chilling from 750° causes little, if any, further alteration in the curve form.

From this discussion of the curves in Fig. 2 it is evident that this method of heating the glass for 15 minutes at 550°C and chilling in

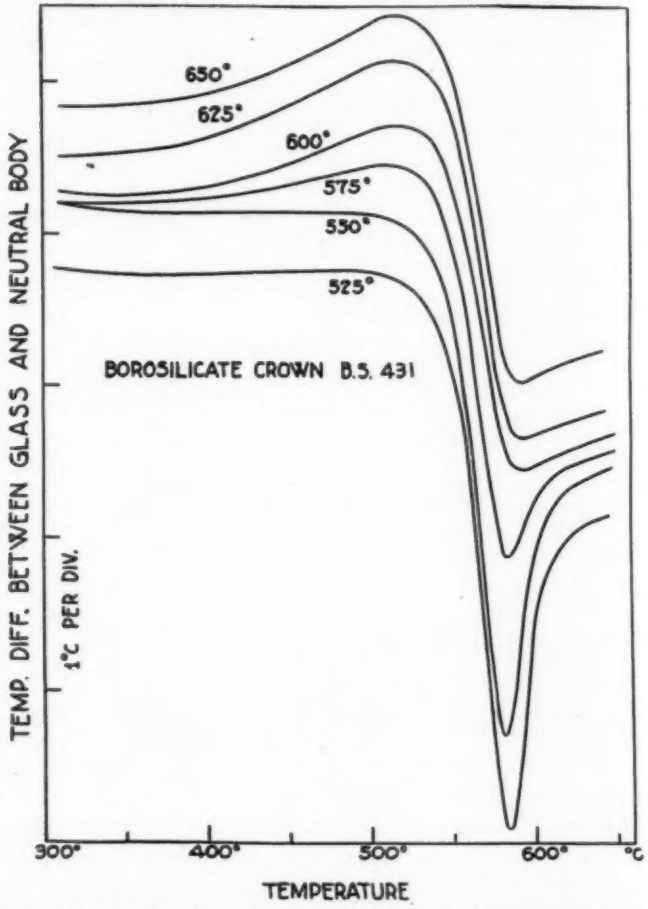

FIG. 2. *Changes in form of heating curves produced by varying the chilling temperatures. Chilled in air after heating for 15 minutes at temperatures indicated.*

air from that temperature leaves it, so far as any observable modification of its heat absorption is concerned, practically unchanged, but that the same treatment for some temperature between 575° and 600°C

produces practically the greatest modification that can be obtained by the use of this particular treatment for any chilling temperature within a wide range.

To vary the treatment water was used as a chilling agent. Since chilling in this manner causes a more rapid cooling through those temperatures where the glass has a considerable mobility and appears to reach with facility new equilibrium conditions, it was thought in accordance with the explanation given in the introduction for the effects produced by rapid cooling, that such a chilling should more fully preserve the effects obtained by the heating treatment. The more effective suppression of the equilibrium changes normal to the range below the chilling temperature produced by the rapid cooling should cause consequently a shifting of those chilling temperatures at which modifications in the curves first become apparent and at which these modifications can no longer be enhanced by further increasing the chilling temperature. In fact, when the series of experiments described in the next paragraph was analyzed and the results compared with those obtained by air chilling it was found that the upper limit, where the effect caused by the combined heating and chilling treatment reached its maximum, was lowered almost 15°, while the lower limit where practically no effect can be detected, was reduced by about 5°C. While these shifts were not large they were quite definite and in the direction to be expected, at least for a glass originally well annealed.

In this particular study of water chilled glasses, curves were obtained for a large number of specimens which were chilled from different temperatures, after the 15 minutes had been allowed as before for adjustment. Since it is difficult to arrange this large number of curves in any manner which would adequately show the changes produced in them by the various treatments, the manner of analysis already described was adopted. The data given in Table 1 represent the averages of the results of this analysis on four or five different curves for each chilling temperature. The returns (d), the drops (b), and the total drops ($a+b$), as given in this Table, are plotted in Fig. 3 against the chilling temperatures.

The temperatures corresponding to A and B determined from the different curves obtained for any chilling temperature seldom deviated from the average by more than 2°C. The deviations in the temperatures corresponding to C were somewhat larger. For the temperature differences corresponding to a, b, c, etc., the deviations from their averages were seldom more than 10% when their magnitude was 2°C,

or more than 20% when it was near 0.2°C. These latter discrepancies were due in the main to the necessity of renewing or disturbing the packing material. It was often possible, however, to obtain practically a complete series of curves for all the chilling temperatures without renewing this material or disturbing it to any extent. In such cases

TABLE 1

Chilling Temp. ±5°C	Characteristic Temperature Difference Variations °C					Temperatures ±5°C			No. of Observations
	Total Drop $(a+b)$	Rise a	Drop b	Return d	Diff. Between Levels c	A	B	C	
Original Untreated	3.98	0.00	3.98	2.09	1.87	550.5	581.5	603.0	4
530	3.94	0.00	3.94	2.00	1.94	550.0	581.0	603.0	5
540	3.96	0.02	3.94	1.87	2.07	549.0	581.5	604.0	5
545	3.91	0.00	3.91	1.83	2.11	549.0	581.0	604.5	5
550	3.61	0.02	3.59	1.52	2.07	549.0	581.0	604.5	5
555	3.33	0.07	3.26	1.11	2.17	549.5	581.5	604.0	5
560	2.94	0.15	2.78	0.91	1.87	549.5	581.5	606.0	4
565	2.74	0.26	2.48	0.59	1.91	550.0	580.5	607.0	4
570	2.59	0.26	2.33	0.30	2.04	550.0	582.0	608.0	4
575	2.65	0.30	2.35	0.33	2.07	550.5	582.0	609.5	5
585	2.54	0.35	2.20	0.22	2.00	551.5	583.0	611.0	5
600	2.70	0.41	2.28	0.17	2.13	551.0	583.5	611.5	4
650	3.04	0.59	2.46	0.15	2.33	553.5	585.5	611.5	4

the curves obtained were similar in all respects to those shown in Fig. 3, except that the ordinates were changed throughout by a constant factor. Consequently in obtaining the forms of the curves in this figure the values of the temperature differences of any such complete series would have served as well as the average values.

Of the three curves given in Fig. 3 that representing the return (d) shows most satisfactorily perhaps the changes produced in the original

curves by varying the chilling temperatures. Since the distance (*c*) between the initial and the final slopes at the point *C* was practically constant, and since *d* was usually equal to *b* minus *c*, the curve for the drop (*b*) has practically the same form as that of the return (*d*). From the figure it will be seen that these curves drop rapidly from the levels for the original glass after they pass 545°, and practically reach a new level at 570°C. The approximate constancy of the ordinates of these curves in Fig. 3 for chilling temperatures above 570° corresponds

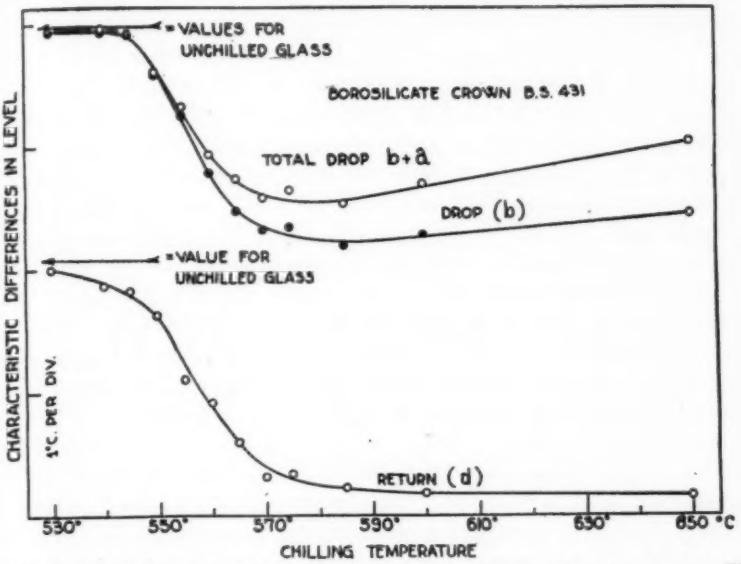

FIG. 3. *Results from analysis of heating curves for glass chilled from different temperatures.*

to the constancy in curve form shown in Fig. 2 in those cases where the glass was chilled in air from temperatures above 600° and even to 750°C as stated in the discussion.

(b) By varying the annealing periods.

As cooling the glass more rapidly produced the results expected and confirmed to that extent the explanation advanced (see page 429) for the effects caused by chilling, it was believed that preheating it for a period greater than 15 minutes would also produce additional confirmatory results, and at the same time furnish data on the original condition of the glass and the manner in which it approaches equilibrium at various temperatures. For instance, if the glass were held for a suf-

ficiently long period at temperatures below the "effective" annealing temperature instead of above it as before, it was thought that the magnitude of the heat absorption as indicated by the drop (b) and the return (d) might be increased instead of being reduced as in the previous tests. This would result in a crossing of those curves for b and d obtained for the shorter treatment by those obtained for the longer treatment.

In these tests the glasses were held for two hours at the chilling temperatures previous to chilling, and the results obtained for the returns (d) and the drops (b) are plotted as curves Nos. 2 and 2′ in Fig. 4. This series of tests was made without any renewal or great disturbance of the packing. The values plotted resulted from single observations excepting in two cases, where they are the averages of two. As it was desired to make a comparison of these results with those in Fig. 3, in order to show the effects obtained by the different periods of preheating, tests were made with this same packing on the original glass. In this comparison the ratio of the values thus obtained for the original glass to those previously obtained (See Table 1) was used to adjust the ordinates of the curves shown in Fig. 3 so that they would be comparable with the others shown in Fig. 4. This adjustment made to eliminate the effects of differences in packing seemed justifiable in view of the fact that as previously stated a new packing merely changed the ordinates by some constant factor.

Since such an adjustment is at best only an approximation it is possible that the crossings of the curves (Nos. 1 and 2) for both the drops (b) and the returns (d) near 520° and particularly at about 570°C are due to this imperfect method of comparison. In order to verify this result for the lower temperature since such a crossing had been expected there, several additional tests, for the same and for longer adjustment periods, were made at temperatures within the range 470° to 510°C. As the facility with which the glass adjusts itself is greatly reduced at these relatively low temperatures, the time required for such tests extends over considerably more than a working day. Since the control of the furnace required adjustment about once an hour for the maintenance of an approximately constant temperature, it was impossible (with the assistance available) to hold the glass at such definite temperatures over the longer periods as for the shorter periods of treatment. But on the other hand, at those temperatures where the mobility of the glass is not great it was believed that qualitative tests of this sort did not require such accuracy of control.

The following is a good example of the procedure in these experiments, and shows a verification of the crossings of the curves. In this test the glass was held 4 hours at 510°C, during the night it cooled at the rate (estimated) of about 1° per hour to 497° and on the following day was held at the latter temperature for 8 hours before being chilled in

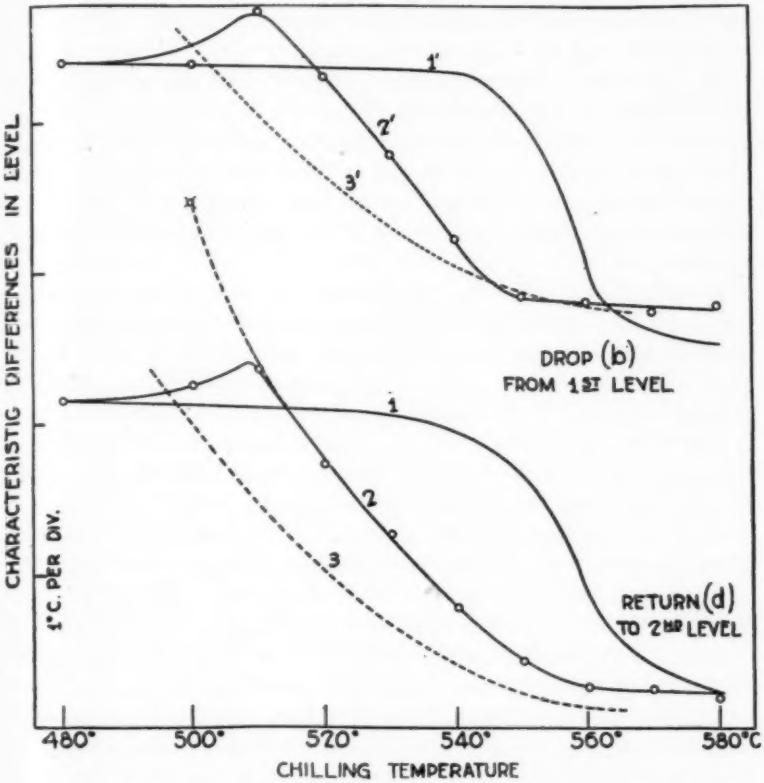

FIG. 4. *Results from analysis of heating curves for original glass after holding at chilling temperatures; for 15 minutes, curves 1 and 1', (adjusted); for 2 hours, curves 2 and 2'; for 25 hours, point on curve 2, extended. Chilled glass reheated and cooled slowly to chilling temperatures, curves 3 and 3'.*

water. The results showed that the drop (*b*) was increased 20% while the return (*d*) was almost 60% greater than that for the original glass. In cases of this sort, comparisons with the original glass were easily made by alternately taking curves on the original and on the treated glasses. If it is assumed that the effective temperature for the

above treatment was near 500°C, the point in Fig. 4 on the dotted branch of the curve for the return indicates the value of d obtained in this test.

All the other tests in which the glass was held for long periods at temperatures below 520°C showed similar results; while all the tests for similarly long periods for temperatures above 520°C showed, on the other hand, that the drop and the return for glass so treated were undoubtedly less than those for the original.

All these tests show, therefore, that the crossing of the curves Nos. 1 and 2 in Fig. 4 near 520°C was not accidental and that this temperature is to be considered as the effective temperature at which the original glass was annealed; that is, this is the temperature at which no further adjustments affecting the heat absorption occur in this glass; or, if such adjustments do occur, then their combined effect must be zero.

If the behavior of the glass approximates in general that previously outlined in the introduction, this type of glass when cooled at extremely slow rates, through the temperature range below 650°C at least, should be in a state that approaches an approximate equilibrium, this state at any time being that which is normal for the glass at the temperature it then possesses. In view of the results so far discussed it is evident that these conditions of equilibrium change markedly through a wide temperature range below 550°. If the glass be cooled slowly enough it should be possible to obtain data on the equilibrium conditions at any desired temperature by immediately chilling a sample taken when the glass reaches this temperature. These equilibrium conditions could then be compared by means of the tests and the curve analysis method described for obtaining curves similar to those shown in Figs. 3 and 4. Furthermore, if the glass is relatively stable, as in this case, these new curves should lie beneath the No. 2 set of curves in Fig. 4 at sampling temperatures above 520°C, cross both sets Nos. 1 and 2 at about this temperature and lie above them for all lower sampling temperatures.

These curves together with data similar to those in Table 1 obtained for a stable glass under standard testing methods should determine the characteristics of the heating curves of the type shown in Figs. 1 and 2 which will be obtained for any and all effective annealing temperatures. This is true irrespective of the annealing treatment given the glass and the treatment previous to its annealing, unless the latter be such as to cause peculiar conditions which once established interfere with

the normal adjustments.[8] Crystallization, for instance, often results in such interference, though it is difficult to say to what extent other transformations may occur causing similar effects.

Certain preliminary experiments of the type just suggested have been made, but as the slowness of the cooling rate in this sort of investigation is limited, it has been impossible so far to test these points thoroughly. In one of the preliminary tests, however, some of the glass[9] was heated to about 600° and cooled from 570° to 500°C at a rate never exceeding 3° per hour. This rate, while greater than that often used in annealing, is at least somewhat slower than that at which the original glass was cooled in the pot. While this cooling cannot give the ideal curves mentioned above, it should at least after proper adjustment has been made for changes in the packing, give curves which for the greater part of this temperature range lie below the other curves shown in Fig. 4, but which at some lower temperature cross them. As expected, the broken curves, 3 and 3′ (Fig. 4), obtained from this test lie below the other curves for a considerable range. They do not cross them, however, until chilling or sampling temperatures slightly below 500°C are reached.

The crossing did not occur nearer 520°C presumably because the rate of cooling was too rapid. In fact, the difference between the actual crossing temperature and the theoretical (that is the effective annealing temperature for the original) depends both on the relative cooling rates and on the magnitude of the adjustments occurring in the original glass at temperatures below the actual crossing temperature. The latter cause is explainable on the assumption that the transformations or rearrangements required for equilibrium at any given temperature may take place at all temperatures below it, much as they do in cases of retarded crystallization. Accordingly, the

[8] There is, e.g., the possibility, if the adjustments are transformations of a chemical nature, that certain intermediate transformations or reactions are necessary to obtain the most beneficial results from annealing. If these occur at high temperatures only, cooling too rapidly through the region above the annealing range may prevent their completion. If they are formed at low temperatures, it may aid annealing (as some think) to cool to room temperature and then reheat the glass to the annealing point not too rapidly. The latter treatment is of doubtful value, however, and even at high temperatures the usual method of cooling should be sufficient. If, on the other hand, the adjustments are purely physical, consisting only of a noncrystalline rearrangement of the molecules into a condition corresponding to the effective annealing temperature, interferences resulting from previous treatments should be even less likely to occur.

[9] This glass had been previously chilled but this fact appeared to have very little significance.

condition of the glass at any time when cooling at any finite rate, will in general correspond to a temperature higher than it then possesses. In this test when the glass had reached 500° its condition corresponded to that for equilibrium at a temperature of 520°C. Since the mobility of the glass was decreasing rapidly through this region, this lag of the temperature corresponding to the condition of the glass will increase rapidly if the glass cools further at a 3° rate; consequently, curves 3 and 3′ should ultimately become parallel to the axis of abscissae.

The test just described shows how the results obtained are affected by the fact that these adjustments of the glass causing the heat absorption effect and requiring considerable time for their completion can occur through a wide range of temperatures well below the usual effective annealing temperatures obtained. An application of the results of this test is found in the case where it is desired to duplicate the effective annealing temperature obtained by cooling a glass at a constantly decreasing rate throughout (similar to the older method of annealing) by treatments in which the glass is cooled more slowly in the upper range and more rapidly later (methods similar to that of Boys[10]). If the latter methods of treatment are to be successful, that is, if they are to duplicate the physical characteristics and the effective annealing temperature obtained by the older method, the cooling rates in the upper range must either be much slower or the slow cooling must be extended well below the effective annealing temperature required. A further discussion of this point will probably be given in a paper to appear later discussing some effects produced by annealing.

2. VOLUME CHANGES CAUSED BY CHILLING AND ANNEALING

If transformations or readjustments of the character discussed in the previous pages actually occur in glass, it appears likely that the density of glass varies somewhat with the treatment. If such changes do occur, there is, however, nothing in the preceding data to determine the direction such changes should take. Nevertheless one should reasonably expect that any density changes resulting from long periods of heating when the treating temperatures are chosen on opposite sides of the effective annealing temperature of the original should have opposite signs. Furthermore, from a study of the changes in expansivity with the temperature it was suspected that cooling rapidly

[10] Boys, Nature, *98*, p. 150; 1916.

after reheating at temperatures above the effective annealing point would reduce the density below that of the original.

A number of investigators have noted certain density variations, occurring usually as the result of rapid cooling or chilling and have ascribed them to different causes. Their results indicate that the density generally increases as the rate of cooling is decreased.

Since the detection of density changes in a glass with treatment, particularly if they should vary with the treating temperature as suggested above, would corroborate the views advanced here, an investigation of this possibility was deemed advisable. Consequently, in collaboration with E. L. Peffer of the Capacity and Density Laboratories of this Bureau, some preliminary tests were made. As a result samples heated for 20 minutes at 650° and 600° and for 2 hours at 550°C, previous to being cooled rapidly in air, were doubly refracting in the approximate ratios of 1:0.5:0.05 and decreased in density by about 1.0, 0.9, and 0.25 per cent, respectively. Several samples heated for long periods at 490°C previous to the rapid cooling all showed, on the other hand, an increase in density approximating 0.2 per cent. These two sets of samples, with densities now appreciably different, were treated together at a temperature near 525°C for about 72 hours and cooled as before. Their densities were then found to be the same within 0.05% of a value about 0.1% lower than the average density (2.564) of the original glass. That the density after this last treatment should be less than the original was to be expected because 525°C is, as shown by the curves in Fig. 4, somewhat higher than the original effective annealing temperature—slightly less than 520°.

It seems improbable that stresses present in the glass could have produced the density changes observed because there appears to be no relation between such changes and the double refraction effects noted. It also seems wholly improbable that stresses of the magnitude and distribution necessary to produce volume changes as great as those obtained could result from the heat treatment given. Furthermore, work[11] by Heyn, Masing and others seems to show that stresses of the character to be expected here should theoretically be accompanied by

[11] E. Heyn u. O. Bauer, Int. Zeitschr. f. Metallographie, *1*, p. 16; 1911.
E. Heyn, Handbuch d. Materialienkunde f.d. Maschinenbau, II. A, pp. 331-363, Berlin, 1912.
G. Masing, Zeitschr. f. Techn. Phys., *3*, p. 167; 1922.
F. E. Neuman, Theorie d. Elasticität, Leipzig, p. 112; 1885.
A. Föppl, Techn. Mechanik, Leipzig, *5*, pp. 236-310; 1907.
A. Föppl, Techn. Mechanik, Leipzig, *5*, pp. 238-310; 1922.

no such volume changes. Apparently then the observed density changes give the expected support to the views advanced, but it appears that they will lend very little aid in determining whether the readjustments are of a chemical or physical nature. It is planned, however, to extend the investigation of these volume changes considerably, in which case they will at some later date be discussed in greater detail.

In view of the magnitude of these density changes it appears reasonable that by varying the heat treatment appreciable changes can also be produced in the refractive index. In fact, variations of this character have been noted by some investigators.[12] The stresses introduced by the rapid cooling, usually required in tests of this character, are such a disturbing factor, however, that it is difficult to determine whether or not the deviations in the index so obtained are to be attributed simply to the strained condition of the glass. Some results published lately by Lebedeff[13] for a glass somewhat similar to that investigated here seem to show conclusively, however, that the refractive index was increased by annealing.

From the foregoing experimental results and discussion, it is evident that those effects occurring as modifications or changes in the heat absorption, density, etc., of the glass and which accompany its annealing and chilling are of a character that may readily be explained on the assumptions that treating at a constant temperature allows the glass to approach an equilibrium condition; while rapid chilling to a temperature where the mobility is very low tends to preserve that condition existing when the chilling began. It is also evident that the condition attained during the annealing period by a glass of given composition is dependent on the annealing temperature and possibly to a certain extent on its previous history. Furthermore, the rate of approach towards the final condition must also depend on these same factors, and, in addition, as experience shows, must increase with the degree of removal from that condition.

[12] See F. Twyman, Jour. Soc. Glass Tech., *6*, p. 45; 1922.

Since this paper was prepared, F. Twyman and F. Simeon have reported to the Society of Glass Technology (See Nature, June 16, 1923) that chilling dense barium crown and borosilicate crown may lower the refractive index by as much as 0.004 and 0.0013 respectively and that annealing removes this effect. They find also that moulding produces a want of homogeneity in the glass which is in agreement with the conclusions arrived at in the article by Tool and Eichlin in the Jour. Opt. Soc. Am., *4*, p. 340; 1920.

[13] A. A. Lebedeff, On polymorphism and annealing of glass. Transactions of the Optical Institute in Petrograd, *2*, No. 10, p. 1; 1921.

So far as the data given here are concerned, the limits of the temperature range within which the equilibrium condition varies appreciably with the temperature, and the temperature at which the glass begins to change appreciably, when it is not in a stable condition, are undetermined. It seems probable that even at room temperature glass may be slowly approaching an equilibrium condition still dependent on the temperature; while at temperatures where the glass is soft the adjustments may all be made so rapidly that the method of attack followed here will not show any evidence of changes in the equilibrium condition with temperature occurring in this upper range. That is, the method of investigation employed here is valuable only in the range where glass has a certain intermediate mobility.

Whether the apparently stable condition reached by a glass held at a given temperature for the periods of treatment possible in an investigation of this sort should be called an equilibrium condition and considered as definite for that glass at that temperature is problematical. A much longer treatment might show that further changes were still possible; also, the effect of the previous history may in some cases be such that samples of the same glass (or of glasses identical in composition at least) differently treated at some stage will reach under identical final treatments different stable conditions. It appears probable, however, that for any temperature in its usual annealing range a glass which has never been mistreated can by proper treatment be brought to a definite, determinable condition of stability. If the glass has a strong tendency to devitrify, it is of course useless to predict what the results of treatments of this sort might be.

IV. DISCUSSION

1. GENERAL REMARKS

In, or possibly somewhat above, the region where the equilibrium condition appears to change most rapidly with the temperature a number of effects, so far not mentioned definitely in this article, have been studied and recorded by several observers.[14] Some of these

[14] M. So, Proc. of Tokio Math. and Phys. Soc. (2), *9*, p. 425; 1918.
W. P. White, Am. J. Sci. (4), *47*, p. 44; 1919.
C. G. Peters and C. H. Cragoe, Jour. Opt. Soc. Am., *4*, p. 105; 1920.
A. Q. Tool and J. Valasek, B. S. Sci. Paper No. 358, Jan., 1920.
A. Q. Tool and C. G. Eichlin, Jour. Opt. Soc. Am., *4*, p. 340; 1920.
A. A. Lebedeff, Trans. Opt. Inst. in Petrograd, *2*, No. 10, p. 1; 1921.
C. G. Peters and C. H. Cragoe, Refractive Index of Glass through the Annealing Range, Meeting of the Optical Society Dec. 27-29, 1920. C. G. Peters, J. Wash. Acad. Sci., *13*, p. 217; 1923.

effects were later observed by Lebedeff, who apparently having investigated but one type of glass, was misled into assuming that they were all related to, if not actually the result of, the $\alpha \rightleftarrows \beta$ transformation in quartz. The glass he investigated was a borosilicate crown, and many of such glasses show a heat absorption effect at temperatures very near that of this transformaton.

The fact is, however, that all the glasses so far investigated in this laboratory—and the number is rather large—show on heating an endothermic effect in some rather definite narrow temperature range, depending on the composition of the glass, and lying within the limits 100° and 800°C. Some glasses may show such an effect outside this range even; e.g., silica glass very probably does so at some temperature well above 1000°C, and quite likely just below those temperatures where it tends to devitrify. Besides, glasses containing no silica whatever show this glass transformation accompanied by all the other phenomena mentioned above at temperatures which seem in no way to be related to the transformation or melting points of the components in any of their known crystalline forms.

In the simpler glasses at least, i.e., in those where the number of components is small, the temperature at which the endothermic effect under standard methods of determination occurs varies in a definite manner, dependent upon the proportion of the components. So far very little data relative to this point have been published, but those given previously[15] for glasses from boric acid, borax, etc., illustrate it. In fact, it may be possible to determine definite transformation diagrams for glasses similar to the solidification diagrams for alloys or salt mixtures.

Since the temperature ranges of these effects in glass are shifted so easily by varying the composition, while the temperatures of the quartz and other transformations in pure crystals (including even that of fusion) are shifted with difficulty, it is doubtful whether the crystalline forms of any of the components of a perfect glass ever play directly an important rôle in the readjustments causing the endothermic effects. Neither does it appear that there is as yet enough evidence to support the belief that any definite crystalline forms whatever exist in a good optical glass, much less that they play a leading part in its normal performances. In view of these facts it appears reasonably certain that the quartz transformation cannot, as Lebedeff

[15] B. S. Sci. Paper 358.

assumes, be related to the normal endothermic and allied effects observed in glass.

The conclusion that glass has no definite crystalline structure and that there is no large number of crystals of any definite type in it seems to be supported by the fact that X-ray tests by various observers[16] have as yet shown no diffraction effects of a character which could be definitely ascribed to crystalline formations. It is quite possible that all the effects so far observed may be explained by the presence of certain molecules, either simple or complex, or molecular arrangements which may or may not have the character of colloidal aggregates. Furthermore, the increase in the fluorescence in annealed glass caused by X-rays and ultra-violet light, which some authorities[17] attribute to a crystalline structure, may also be explained by molecular readjustments or the formation of compounds having more complex molecules. It appears at present that the question of the character of the molecular adjustments in the glass causing the various effects discussed may be decided most easily by means of X-ray analysis when this method[18] of attack is sufficiently extended.

Such effects, as the absorption and evolution of heat and the variations in the specific heat, plasticity, expansivity, density, refractive index, etc., can doubtless be explained also by molecular readjustments or changes in certain compounds or molecular aggregates. These changes produced by varying the temperature or treatment may be simply progressive readjustments in the molecular arrangement or they may include a change in the relative proportions of the different compounds or aggregates always present, and to a degree, changes in their physical and chemical properties. The formation of entirely new compounds or aggregates, or the complete destruction of old ones may also occur. Such changes may include, of course, crystallization of certain components, but ordinarily, when this begins it indicates the deterioration of the glass.

[15] R. W. G. Wyckoff, Amer. Jour. Sci., *5*, p. 455; 1923.

C. V. Raman, Nature, *111*, p. 185; 1923.

E. Huckel (Phys. Zeits., *22*, p. 561; 1921) and others discuss what may be similar diffraction effects in liquids.

[17] Sir Herbert Jackson, J. Roy. Soc. Arts, *68*, p. 134; 1920.

[18] To determine whether the diffraction effects for X-rays produced by chilled and annealed glasses differed greatly, powdered samples suitable for such tests were prepared. R. W. G. Wyckoff, of the Geophysical Laboratory of the Carnegie Institution of Washington, who kindly consented to perform these tests, has reported that these samples showed the usual diffraction effects peculiar to glass, but that there was no apparent difference between the chilled and annealed samples.

The manner in which any molecular readjustments or the formation and destruction of any aggregates or compounds may affect the properties of glass, particularly its plasticity and deformability, has been fully discussed in a previous paper. The views advanced then have not materially changed, and involve little more than an application of the Maxwell-Butcher theory[19] designed to explain, on the basis of "molecular groups," certain phenomena observed when materials are deformed. Consequently, a further discussion of this phase of the problem may be omitted except to state that the results of the present investigation make it evident that such aggregates or substances if present are formed not at any definite temperature but that either their number, their character, or both, vary when the temperature or treatment is changed. The conditions which require changes of this sort if the formation of aggregates is to explain the results observed must also be imposed on any other type of readjustment of the molecules to a more stable position with long annealing if it is to give a satisfactory explanation.

If the readjustments on heating and cooling continue normally over such wide temperature ranges as indicated by tests described here, it may on first thought appear difficult to explain how any clearly defined endothermic and exothermic effects can arise from these actions. This is particularly true in the case of the sharply defined absorption effect in well annealed glasses. From the data presented it is evident, however, that an undercooling, which appears quite natural if an aggregation of any character tends to occur, is obtained by chilling the glass, apparently because the low mobility hampers all readjustments. It is equally certain that a superheating will be obtained by heating rapidly. In this case it may well happen that the molecular arrangements in the superheated glass break up very rapidly within a rather narrow temperature range and consequently produce a sharply defined endothermic effect.

In regard to the exothermic effect on cooling[20] it should be remarked that it is so lacking in sharpness that few have detected it. This is to be expected if the transformations proceed for a time gradually and normally as the temperature is lowered, and then after an intermediate period cease almost completely when the mobility becomes too low. The heat effect observed on cooling is explained therefore by the

[19] Butcher, J. G., Proc. London Math. Soc., *8*, p. 103; 1876-77.
[20] B. S. Sci. Paper 358.

relative rapidity with which the mobility reaches a value causing the almost complete cessation within a narrow temperature range of any exothermic transformations occurring normally at these or at higher temperatures (if any such are still incomplete because of a too rapid cooling). The difficulty of detecting this phenomenon arises from the fact that the observable effect is not sharply defined, being caused only by the gradual ending of a series of exothermic transformations or readjustments. Cooling more rapidly merely raises the temperature at which the actions are halted, consequently suppressing a larger number of transformations. These readjustments suppressed by rapid cooling give rise to the exothermic effect on reheating. This latter effect is not so clearly defined as the endothermic effect on heating, but is more pronounced than the exothermic effect on cooling, because it results both from the beginning and ending of a series of exothermic transformations, and is followed by the endothermic effect.

These considerations show that all the observable effects are in reality due to the rapid change in the mobility in what may be considered as a boundary range. Above this range the changes necessary to reach an equilibrium proceed with ease and in doing so allow some type of aggregation to proceed possibly from the time the glass begins to cool in the pot; but below it, although the tendency for these changes still exists, they are almost wholly suppressed by the elastico-plastico-viscous properties of the glass. This is the explanation which the forms of the heating and cooling curves suggest.

This reversible process in which aggregates or compounds build up on cooling and disintegrate on heating may constitute merely the slow readjustment of some or of all the components of the glass into a more or less compact arrangement; it may be some reversible chemical reaction between two or more components; or it may even be similar to some of the processes observed in solutions. If either of the two latter possibilities are assumed to give the correct explanation for the heat effects observed it is still difficult to predict what the substances or compounds may be which are involved. It appears, however, that they must be made up of the more complex molecules existing in the glass.

Such an explanation is more or less in line with the theories of Zulkowski[21] and others who relate the durability and certain other

[21] Karl Zulkowski, Chem. Ind., *22*, p. 280; 1899.
Chem. Ind., *23*, p. 346; 1900.
W. L. Baillie, Jour. Soc. of Glass Techn., *6*, p. 68; 1922.

properties of a glass to that degree to which its treatment and chemical constitution allow the proper formation of double silicates, etc. It is true that in these theories the formation of the substances is usually assumed to occur in the fining stage, although it has been suggested that they may occur to some extent in the annealing range. If, however, the transformations of these substances are to explain the results of this investigation, it must be assumed that their formation occurs throughout the whole cooling period or at least until the rigidity of the glass prevents it; and further, if the cooling is slow enough that practical equilibrium is maintained between the simpler and more complex molecules or aggregates, although their relative numbers vary with the temperature.

2. PRACTICAL APPLICATIONS

Assuming that the readjustments in a glass on cooling produce, in general, an increased stability, it is still possible, unless the composition is correct, that their occurrence may cause at times a segregation or formation of some undesirable component, which may lessen the durability, cause a coloration, or produce a tendency to crystallize. In the case of colored glasses and those similar to opals, these effects may be desirable, but in general they are not.

In fact, the heat treatment received in or near the heat absorption range affects the colors in some colored glasses. Other glasses, certain opals in particular, show very peculiar heating curves with apparently two or three more or less distinct regions of heat absorption. Still other glasses become white on reheating or on slow cooling through temperatures above the heat absorption range, and have entirely different ranges in the transparent and translucent states. All the glasses[22] so far tested which crystallize at all do so first at temperatures

[22] Relatively simple glasses in which this effect can easily be shown are those from sodium metasilicate and from borax. Curves taken on the former showing the relative position of the endothermic effect of the glass and the exothermic effect of crystallization are given in B. S. Sci. Paper No. 358. In the case of the latter glass, data, also given in that paper, show that the endothermic effect begins at 450° and ends at 480°C, while the work of Day and Allen published in "The Isomorphism and Thermal Properties of the Feldspars," Carnegie Institution of Washington, 1905, indicates that crystallization cannot be induced below 490°.

At this point it may be added that Adams and Williamson in "The Annealing of Glass," Jour. Frank. Inst., 1920, appear to confuse the heat absorption recorded in the Bureau of Standards paper mentioned with that effect observed by Day and Allen in borax glass around 500°C. This, however, is about 20° above the end of the normal endothermic effect in borax glass. Furthermore, from the diagram of the apparatus used by the latter authors it would appear that the effect they mention was of the nature of the variations in the heating

well above the first endothermic effect on heating. These facts indicate that the durability, stability, coloration, etc., may be influenced by those readjustments which have been assumed to be responsible for the heat effects. From practical considerations it might be advantageous, therefore, to pursue the study of this phase of the problem much further than has yet been possible.

Rearrangements of any character, whether they result merely in increasing the compactness of the molecules or in the association of several molecules into complexes with their possible resultant interlacings, will greatly decrease the mobility through increasing the viscosity and probably by causing plastic effects. In temperature ranges where the molecular freedom is rapidly reduced through increasing the molecular compactness or the rapid formation of large complexes, the deformability of the material will be reduced rapidly, and if this continues practical rigidity will soon result, suppressing further readjustments. If these readjustments are related to the observed heat effect, and if their character, extent, and tendency to occur do not differ too greatly from glass to glass, the mobility as determined by the deformability under stress should in the range of these heat effects be about the same for many glasses.

It is apparent then, why the determination of the temperature ranges for the endothermic effects may be of great aid in locating the proper annealing temperatures of glasses. This was discovered very early in these investigations, as shown in B. S. Sci. Paper No. 358. Thus the annealing temperature must be such that the stresses may relax, and that a sufficiently uniform equilibrium may be established in a reasonable time, and also such that the cooling may then proceed at a reasonable rate without introducing undesirable permanent strains due to the unavoidable temporary stresses incurred in this process. In addition, the cooling must also be at a rate that will

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rate often observed in this laboratory when the glass begins to soften, as stated on page 425. For even when precautions were taken to insure that the thermocouple wires and protective tubes were not conducting heat to or from the glass too rapidly, slight apparent exothermic or endothermic effects were noted at the sintering point, i.e., when the glass surfaces soften enough to stick together slightly or to the wires and tubes. It was assumed, therefore, that these effects were caused by changes in the conductivity due to a tendency of the glass, if powdered, to collapse and to leave the walls, or, particularly when unpowdered, to the formation of a better contact between it and the thermocouple parts. In the former case and also in the latter if the junction were at a slightly higher temperature than that of the glass, an apparent endothermic effect would probably result. According to Day and Allen, the effect observed by them was in the sintering range.

allow the transformations to proceed towards a degree of completion that insures the stability and characteristics required. A consideration of the form of the heating curves both before and after annealing and a determination of the temperature at which the heat absorption occurs are of great aid in meeting these fundamental requirements.

The deformability in the heat absorption region naturally varies somewhat from glass to glass. In the same glass it appears to differ somewhat with the load, method of application, and previous treatment of the glass. In general, however, bending tests show that a strip $100\times10\times1$ mm supported at the ends and loaded in the middle with 100 grams will fall in the middle at a rate of approximately 12 mm per minute when held at a temperature corresponding to the end of the heat absorption range and at a rate of about 0.46 mm at the beginning, although such values for some glasses may differ by a factor at least as great as ten from these approximate means. The above values give for Maxwell's constant[23] the approximate results, $ET=3.5$ and $ET=91.0$ respectively, where E, the elastic coefficient, is expressed in kilograms per square millimeter, and T, the relaxation time, in hours. These values of ET are such that an annealing time of five minutes should reduce the stresses in the glass to less than a hundredth of their original value.

The temperatures in the range of the endothermic effect are higher, therefore, than are required for merely removing stresses. For this reason in the previous articles the annealing temperatures recommended for removing stresses were chosen some 20°C below the beginning of this range. However, as it was suspected that equilibrium was lacking in chilled glasses and that inhomogeneities existed, it was suggested that a glass should be heated for a short time to temperatures within this range before holding it at the chosen annealing temperatures. This treatment was suggested because it was not known whether adjustments of this type could be attained at a given temperature as easily as the removal of the stresses.

Such inhomogeneities[24] resulting from the equilibrium conditions varying throughout the glass accompanied, as they evidently are in

[23] Clerk Maxwell, Phil. Mag. (4), *35*, p. 129; 1868.
Collected Papers, Univ. Press, Cambridge; *2*, p. 30; 1890.
Obviously the simple relations employed here do not fit exactly the conditions met with in glass, but as Twyman (Soc. Glass Techn., *1*, p. 61; 1917) has shown, tests of this character aid greatly in determining the proper annealing temperature.

[24] Some tests on unannealed moulded blocks have indicated, to a certain degree, inhomogeneities of this character, since samples taken from the center and near the surface gave slightly different heating curves.

view of the preceding results, by volume and index differences, will produce poor definition in optical glass. Quite possibly they have in many cases been partly responsible for this effect when it was ascribed wholly to strain. In annealing the differential volume changes which the inhomogeneities produce may cause the stresses to relax at an apparently different rate (either faster or slower) than the known mobility of the glass would warrant. In cooling, since such inhomogeneities are usually associated with different expansivities, permanent stresses may be built up in glasses which were almost stress-free when the cooling began, tensions often being introduced in the final product in regions where compressions would normally have been expected. Such effects in optical glass lower its quality and produce erratic results in annealing, similar to those resulting from almost if not wholly invisible striae and cords and also from surface changes and particles introduced in the working of the glass.

In rapidly cooled glass differential volume changes due to such inhomogeneities may cause even at room temperature marked redistributions of the stresses and increases in their magnitude sufficient to bring about spontaneous breakage. Furthermore, when the glass is in a reasonably uniform condition, it may, if its parts are held at widely different temperatures, undergo differential changes which under certain conditions of rigidity and treatment[25] also cause breakage.

Continued alterations in the equilibrium conditions of the glass, if accompanied by volume changes of the order found, would obviously be a serious disturbing factor in thermometers and high precision volumetric apparatus, particularly if such changes proceed at an appreciable rate at ordinary temperatures, or in case the piece of apparatus is occasionally raised to temperatures where the effects

[25] Consider, for instance, a large concave glass mirror such as is used with searchlights and which is in equilibrium at about 500°C—this is lower than was found by actual test to be the case for some mirrors. In use the mirror edges are probably not much above the normal temperature of the surrounding air, but the center near the arc is very much hotter: consequently, the center is greatly expanded relative to the edges. In the first place, the stresses so caused produce permanent strains more rapidly at the center than at the edges since the mobility is higher there. In the second place, the equilibrium conditions also change much more rapidly there for the same reason. Both effects in time cause the center to become too small for the outer ring when the glass cools. Tensions then result, particularly at the front surface near the lamp, reaching a maximum after the mirror has cooled for some time. If they are great enough (and they need not be large if the surface is scratched), the mirror breaks. Which of the two effects is the more potent is not known, but the latter can be decreased by lowering the effective annealing temperature, and both can be reduced by keeping the mirror at a uniform temperature.

become more pronounced. In the case of a thermometer, if it be heated for a time above the effective annealing temperature and cooled rapidly, its volume will be increased and the reading at the ice point consequently lowered. On the other hand, if it be held for a considerable time (which must be considerably longer than the original annealing time) somewhat below the effective annealing temperature, its volume will be decreased and the ice point reading raised. The troublesome ice point fluctuations usually attributed to stresses may be to a considerable degree the result of such volume changes.

These are a few of the points where the results of the present study appear to bear on those obtained in practical experience with glass. It is true that somewhat similar explanations have been advanced before, although not generally accepted. It is significant, however, that data so strongly corroborative as those given here can be obtained by this method of attack.

V. SUMMARY

The view is advocated that at every temperature glass tends toward an equilibrium condition which is a function of that temperature. While the condition of perfect stability at room temperature may never be reached, because the mobility of glass becomes too low, it is shown from the results of experiments that what appear to be stable conditions for given temperatures are approached with rapidity at temperatures slightly above the usual annealing range.

In procuring the data on which this conclusion is based heating curves were obtained on samples of glass, each of which had received one of a number of different annealing and chilling treatments.

A method of comparing these curves was devised to show more clearly the effect of these treatments on the characteristic heat absorption and evolution effects in glass.

It was also found that the density of the glass in agreement with the above view differed markedly with the treatment the glass had received, and that the treatment required to produce either an increase or decrease in the volume could be determined from a study of the heating curves.

The effects observed are discussed in detail, the conclusion being that they result either from the continual formation of more complex molecules or aggregates or from the general tendency of the molecules to assume a greater compactness as the temperature is lowered, and from their disintegration or separation on heating. Such transforma-

tions coupled with the tendency of these substances to become superheated or undercooled because of the low mobility of the glass are shown to be sufficient to explain all heat effects observed in the annealing region.

Mention is made of the bearing of the results of this investigation on problems in practical glass manufacture involving the durability, stability, deformability, coloration, crystallization, homogeneity, and such heat treatments as annealing and hardening. The possible relation between the volume changes observed and the ice point fluctuations in thermometers and the breakage of unequally heated glasses, such as searchlight mirrors, is also pointed out.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

Series in Spectra of Ionized Elements.—These papers by Fowler and by Paschen represent work of the highest skill carried out in a difficult field, and the results furnish a striking and important confirmation of Bohr's atomic theory. Spectroscopic series were first discovered in the spectrum of an ionized element, by Fowler in Mg, in 1914, and it was then apparent that by having lost one electron the atom of magnesium became similar in spectroscopic properties to the atom of sodium. Bohr was able to show that the wave numbers of the lines of such series should be representable by spectrum series formulae of the usual sort, except that in place of the series constant N, the quantity $4N$ should enter, if the atom were singly ionized; $9N$ if doubly ionized; and $16N$ if it had lost three electrons. Fowler's series in Mg were of the $4N$ type, and now Paschen has found series of triplets requiring $4N$ in the spectrum of singly ionized Al, and of pairs in doubly ionized Al to which $9N$ applies; while Fowler's results show that $16N$ series exist in trebly ionized Si. These new series are not otherwise very different from the ones already known. The four sorts of atoms, normal Na (Na I), singly ionized Mg (Mg II), doubly ionized Al (Al III), and trebly ionized Si (Si IV) resemble each other closely in having one external electron only, though their nuclear charge is different. Their spectra are closely similar, except for a general and regular shift toward the higher frequencies with increase in the nuclear charge. The lines in nearly all these series occur in pairs, and the separations between the lines of a pair are characteristic of each element, and vary in a regular way throughout the set. No simple laws have been found, however, to express any of these changes. To illustrate the shift of the spectrum from one element to another it is sufficient to mention the most important lines in each of these spectra, which occur as follows: Na I near λ5890, the well-known D lines; Mg II near λ2796, Al III near λ1854, and Si IV near λ1394, thus reaching far into the Schumann region; while the separations of the pairs on a wave-number scale run 17.2, 91.5, 238, and 460 respectively.

The experimental side of these researches is very difficult, the chief practical problem being to sort out of any spectrum the lines due to the

element in a particular stage of ionization. Paschen accomplishes this for Al by using a hollow cathode in a vacuum tube, and observing that this form of tube, with an atmosphere of He and Al terminals develops lines of Al I and Al II only, while a violent spark between pieces of Al brings out other lines in addition, shown to belong to Al III. Fowler observes the lines of Si IV in the most violent discharges, and in the spectra of the hottest stars. He has not yet completed the task of disentangling the spectra of Si II and Si III.

Paschen finds in the spectrum of Al II a close analogy with Mg I, though they differ in some small details. In particular, the diffuse series presents novel features in that the "satellites" by which the heavy lines are accompanied, occur here on the opposite side from usual; and in the fundamental ("Bergmann") series the spacing of the triplets changes in an abnormal manner.

In all the spectra of these ionized elements there are found series of four types, as is usual, and also of a fifth and even of a sixth type, resembling more and more closely the series of hydrogen in the spacings of the lines. Doubtless these are to be explained as due to electrons which are describing orbits exterior to those ordinarily followed, and thus residing at some distance from the rest of the atom, which then acts more and more like a point charge, as occurs in the case of H. Such orbits should be found in ordinary spectra, but would be expected to produce lines in the infrared where they have not yet been observed.

We should welcome further work in this field, as it seems to offer a convenient means of studying the nature of these temporary and incomplete atoms. [A. Fowler: The Series Spectrum of Trebly-Ionized Silicon. Proceedings of the Royal Society, A *103;* p. 413; 1923. F. Paschen: The Spark Spectra of Aluminium, Annalen der Physik, *71*, pp. 142 and 537; 1923.] F. A. SAUNDERS

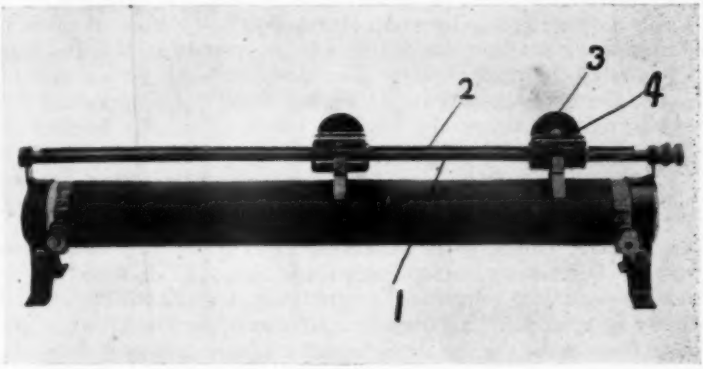
Adjustment of Long Focus Cameras.—The adjustment of a camera includes the finding of the point at which the axis of the objective pierces the plate, the adjustment of the plate to perpendicularity to this axis, and focusing. The author has in mind particularly the needs of topographical and astronomical photography. The axial point is found by aligning the images formed by the various surfaces of the lens using a source especially designed for the purpose. Perpendicularity of the plate is established by stopping down the objective to a very small aperture and then aligning this stop with the image of the pupil of the eye as seen in the reflection from a glass plate placed in the plate holder. The focusing is done by a modified "Hartmann" method in which a "tube collimator" is used. This is a simple device that gives a pair of parallel narrow beams. It consists of a tube carrying at each end a metal plate having two small perforations, the two plates being alike and so adjusted that the line joining the two holes in one plate is parallel to a similar line on the other plate. [M. J. Baillaud, Revue d'Optique, *1*, pp. 353-362; 1922.] G. W. MOFFITT

INSTRUMENT SECTION

AN IMPROVEMENT IN THE SLIDE WIRE RHEOSTATS

By Enoch Karrer and A. Poritsky

In working with slide wire rheostats one frequently encounters the annoying circumstance of the slider sticking to the guiding rod or to the resistance wire. In order to move the slider it is necesszry then to hold the rheostat or else to have it fastened to the table. Also, under these conditions it is no easy matter to move the slider by very small steps as is frequently necessary. These difficulties are



entirely done away with when the guiding rod is provided with a rack and the slider with a pinion. The accompanying figure makes the matter very plain. The guiding rod (1) was grooved out and a rack (2) soldered in the groove. The slider is now movable with ease by turning the milled head fiber disc (3) attached to the pinion (4). We found this improvement very convenient in connection with the resistance previously described by us.[1]

Nela Research Laboratories of the National Lamp Works

[1] E. Karrer and A. Poritsky. An Improved Slide Wire Resistance. J. O. S. A. and R. S. I. 7, p. 277; 1923.

Diffraction of X-Rays by Liquids.—An investigation of the molecular structure of some liquids which would presumably be simple, by the method of Debye and Scherrer. The liquids were oxygen, argon, benzene, ethyl alcohol, ethyl ether, and formic acid. The X-rays were filtered to bring out the $K\alpha$ line ($\lambda = 1.54$ A) of the copper anticathode. The diffraction patterns show in general one strong ring, indicating, on the basis of a treatment given by Ehrenfest for systems of two or more equidistant particles, a distance between the particles of from 3.75 to about 6 A. These distances agree with the distances between centers of molecules for closest packing calculated from the number of molecules present in the liquid, suggesting that the pattern observed results from cooperation of adjacent molecules, rather than from the equidistant atoms of diatomic or polyatomic molecules. For some liquids, surrounding the strong ring there is a weaker one, corresponding to a distance between particles of about 2.4 A. It is suggested that this may indicate groups of atoms arranged as body centered cubes, the two rings corresponding to diffraction by the planes parallel and diagonal to the edges, respectively. The forces causing such a structure might be the forces causing crystallization when the temperature of the liquid is reduced below the freezing point. [W. H. Keesom and J. DeSmedt, Journal de Physique et le Radium, *4*, pp. 144-151; 1923.]

P. MERTZ

An Electric Clock with Detached Pendulum and Continuous Motion.—Describes a mechanism connecting a pendulum and motor in which the pendulum is made to control the motor without the use of the ordinary escapement. Impulses are given to the pendulum by a "gravity arm," which, at the end of the impulse is arrested by a fixed stop, with which the arm makes electrical contact thereby short-circuiting a resistance in series with the motor and allowing an "impulse" to be given to the motor. The motor drives, through a reducing gear, an eccentric cam which, by means of a suitable lever raises the gravity arm in position ready for the next stroke, thereby breaking the "short-circuit," and allowing the motor to run by its own inertia and the small current through the resistance in series with it. Should the speed of the motor decrease slightly, the duration of the electrical contact is longer and speed is brought up to normal; conversely if the motor is running too fast. The motor, thus running at constant speed, may be used to drive clock hands, telescopes, chronograph drums, etc. A 20 pound pendulum clock, of this design, is described, the motor of which uses only .01 watt, and which frequently keeps time to one-half second per week. A heavier duty turret clock, with a 1/25 H. P. shunt wound motor, experienced no disturbance when a torque of 56 lb. ft. was applied to the hands. [Alex. Stewart, Proc. Roy. Soc. Edinburgh, *43*, pp. 154-159; 1923.]

F. K. RICHTMYER

WOOD'S METAL AS A SEAL IN VACUUM APPARATUS

By Lars A. Welo

I had occasion last spring to seal a small plate of crystal quartz to the partially closed end of a glass tube. To avoid the possible presence of vapors from waxes and cements, the method recently described by Farnsworth[1] was adopted of first platinizing the glass and quartz, plating with copper, and finally soldering the parts with Wood's metal. The plan had to be abandoned since an adhesive layer of platinum could not be put on the quartz plate at any temperature short of fusion. Fusion of the plate would have spoiled it for the purpose in view; namely, transmission of the ultraviolet down to 1500 A.

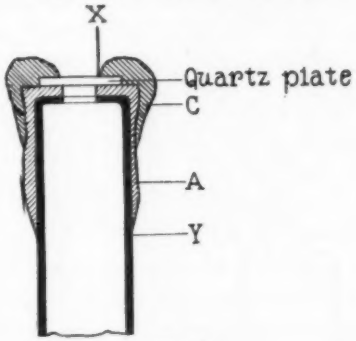


Fig. 1

The plan illustrated in Fig. 1 was then proposed. The glass tube was to be plastered with Wood's metal, as shown at *A*, the top filed flat as a seat for the plate, and more metal piled around and over it, as shown at *C*. It was expected that a small amount of wax along the edges at *X* and *Y* would be necessary as a final seal, but that the wax would not be injurious, since the vapors would diffuse through the narrow space between the metal and the quartz at a very low rate as compared with that of pumping.

It was surprising to see how well Wood's metal molded itself on and adhered to the glass and to the quartz. The tube was therefore tried without applying wax at *X* and *Y* and was found to be free of any leak whatsoever. It was evident, then, that Wood's metal, when applied directly to glass or quartz, molds itself and adheres sufficiently well to prevent the passage of gas along the interface and that it lends

[1] Phys. Rev., *20*, p. 361; 1922.

itself to use as a general substitute for wax or cement in closing joints or attaching plates.

The method has since been used for both types of seals represented in Figs. 2 and 3. The parts are thoroughly cleaned and the metal smeared on with a soldering iron to a thickness of two or three milli-

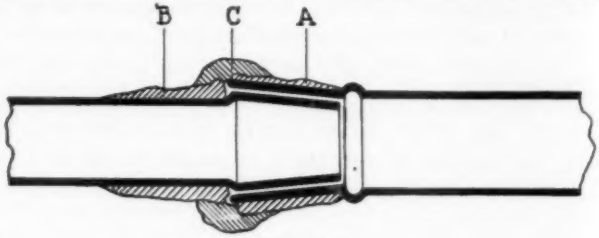


FIG. 2

meters, as shown at *A* and *B*. No flux is necessary or desirable and on account of the low melting point of Wood's metal there appears to be no danger of cracking the glass. The parts are then soldered together with the same metal, as shown at *C*. If the tube be found to leak, it is most probable that it is due to imperfect joining of *C* with *A* and *B*. In no case among the several seals made was there any leak along the

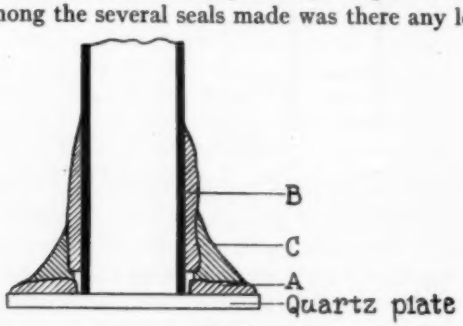


FIG. 3

interface metal-glass or metal-quartz. The leak could always be remedied by resoldering at *C*. It is evident that the portions of metal *A* and *B* may remain permanently. The seal can be opened and closed repeatedly by simply melting off and resoldering the junction. It is also evident that by properly fitting the surfaces to be joined and applying the Wood's metal only to the outside, the rate of diffusion to the evacuated space of the vapors of the metal constituents of Wood's metal may be made very small indeed.

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AN APPARATUS FOR OPTICALLY RECORDING THE PROPAGATION-VELOCITY OF MUSCLE CONTRACTION WAVES*

By Samuel E. Pond

This paper describes a device which optically registers a contraction wave as it reaches different points along a muscle. Such an apparatus has been used in determining the velocity of the contraction-wave of muscles excised from the body of different animals, and is adaptable to use in the study of muscles, the contraction-velocity of which varies within quite wide limits.

The thickening of an activated muscle is employed to tilt minute mirrors, arranged so that the reflected beams of light affect a moving photographic film. The deflections of each beam are thus recorded in the form of curves upon a photographic surface. The muscles are arranged in both horizontal and vertical positions on supports which are without physiological effect upon the tissues and which readily permit quick and complete changes of solutions about the tissues. The illumination of the mirrors is by one arc lamp with adjustable slits arranged with an electrically operated shutter.

Muscle Element: A relatively small muscle is fastened to a specially constructed element made of Bakelite-Dilecto (a vulcanized fiber impregnated with the reaction-product of phenol and formaldehyde). This material is not toxic to tissues in contact with it, at least for ninety-six hours. The muscle-element (*cf.* Fig. 1) is made of two apposed sheets of Bakelite-Dilecto, 1/8 inch thick. One sheet is slotted and beveled to form a guide-way, in which slides a muscle-table; the other sheet is not so slotted and forms a back plate. At B_1 and B_2 rectangular holes are cut through the sheets. Step-bearings are made from 1/4 inch sheeting by drilling a little way into one face of the head of each step-bearing block as indicated in insert *C*, at *Sb*. Each block is then drilled completely through at *h*, and when it is placed in position as at B_1 a bakelite wedge behind the back plate holds the bearing in plate. Screws which support the stud, shown in insert *F*, further clamp the two Bakelite sheets together.

Upon the supporting board (*cf.* Fig. 1) are mounted two shafts (*S* and *S'*) rotated by levers (*L* and *L'*) which come in contact with the muscle placed on the table (*T*). At the top of the element are small metal ribbons (*R* and *R'*) supported by clamps at each ribbon-end,

* Based upon experiments of the writer when Fellow in Biology in Clark University, Worcester, Mass.

under an adjustable tension. German-silver arms (A and A') extend from the shafts and are in contact with the tension ribbons so that as the muscle displaces the levers resting upon its surface the ribbons are slightly twisted about their long axes. Stepbearings below and pointed Monel-metal screws above support the rods and permit free rotation. The muscle on the table is held isometrically, since both extremities

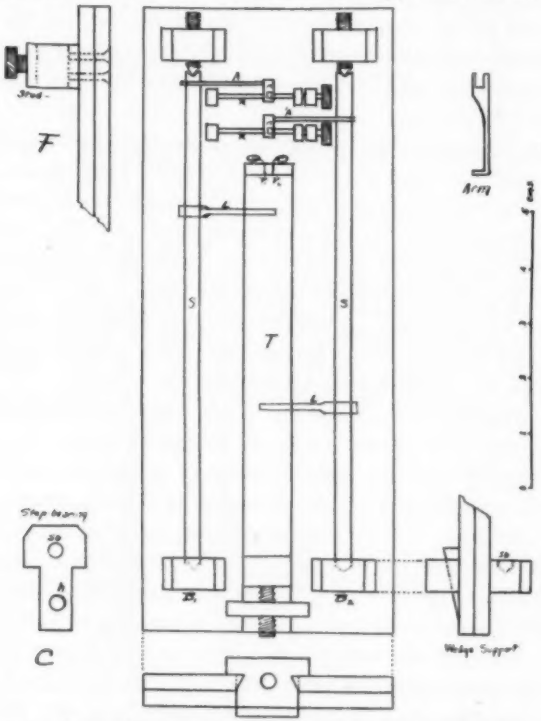

FIG. 1. *Contraction-wave indicator for small vertically supported muscles*

are clamped between the beveled edges of small pieces of the supporting material and the ends of the table, and firmly held in position by pressure from a threaded rod shown as Sc (Fig. 1). The whole element is supported vertically by a stud and clamp (shown in the insert F) by a rod and adjustable stand not indicated in the drawing and provided with a three-way movement.

The muscle levers L and L' are made from strips of 1/8 inch sheet Bakelite, drilled through one end and fitted closely to the shafts. Each lever is shaved down where it projects over the muscle-table and one edge (which rests upon the tissue) is sanded to a V-shape.

The arms A and A' are made of German-silver strips 0.5 mm thick and 3 mm wide, one end being slotted and fitted into grooves cut across the shafts, so that they project edgewise from the shafts over the tension ribbons. The metal of each arm is cut away to form a finger-like device, the small projecting part engaging a portion of the tension-ribbon.

The metal ribbons R and R' are made of German-silver rolled flat from spring wire to about 0.09 mm thickness, are cut to strips 3 mm wide with two side ears near the middle of each ribbon, about 1 mm square. Each strip is held in place at both ends by small clamps, one of which is movable, in a small stock, and is under tension from a coiled spring between a knurled nut and the stock. The tension of the ribbon may thus be altered by turning the nut in one or the other direction.

The mirrors, M and M' are made about 1 mm square in size and from a thin lens ground for the working distance. The concave side is silvered, by supporting it in a conical paraffin bath, flowing the solution under the lens until it is uniformly wetted and permitting it to remain quiet for a half hour or more. The mirror when dried is placed, silver side down, on a block of "Art Gum" or blotting paper and scored into small squares with a "diamond." Firm pressure in different places will cause fractures thus separating off small mirrors. The glass side of the pieces is fastened to the metal ribbons by beeswax.

In use, a strip of muscle, like the sartorius of a frog, is placed upon a "table" slightly shorter than the tissue, and the extremities clamped between the beveled edges of the table and support. The screw (Sc) is used to clamp the parts in position. Each shaft is now placed in its step-bearing in such a position that when the upper arm (extending from the upper end of the shaft) engages the tension ribbon the knife edge of the lever just rests upon the tissue. Since the lever is held to the shaft by friction this position is easily attained. The Monel-metal screw is then adjusted so that the shaft is centered and rotates freely. The whole device is then clamped to an apparatus-stand and a tumbler of solution is raised about the tissue from below. Induction shocks are applied to the muscle through platinum points, indicated as P_1, P_2 in Fig. 1. The resultant thickening moves the levers where they rest upon the tissue and thus brings about consequent tilting of the mirrors. The deflections of the light beams from their original position are recorded on a sensitive film supported in a simple camera.

The contraction-wave of large tissues such as the heart of Limulus may be more satisfactorily studied when horizontally rather than vertically supported. For this position an optical element of a different form suggested by Dr. Louis K. Thompson[1] is employed which

[1] Formerly Fellow in Physics, Clark University, Worcester, Mass.

is placed above the tissue and lowered into position by a rack and pinion. A forked element of brass indicated in Fig. 2 supports a tension ribbon in such a position that an upward movement of a contact-pin tilts the mirror forward. The tension of the ribbon is adjusted by the knurled nut T which presses against a coiled spring between the nut and stock. The contact-pin is T-shaped, made from thin walled tubing 0.45 mm diameter, of an aluminum alloy and fitted to a thin

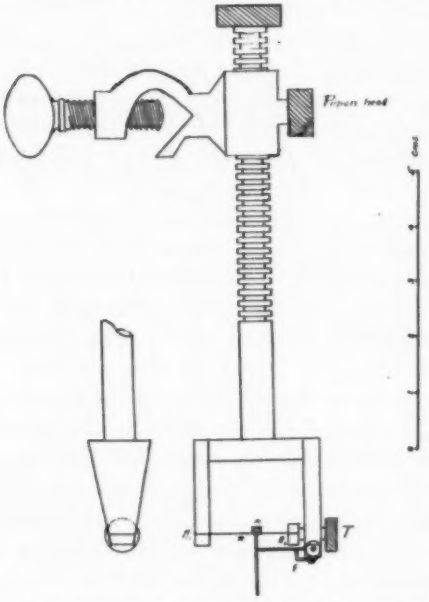

FIG. 2. *Contraction-wave indicator for horizontally supported muscles*

Monel-metal disc, 3 mm diameter in the center of which is mounted a watch jewel, pierced in its center and mounted upon a slender Monel-metal shaft. The rotation (at f, Fig. 2) is limited by a stop, which may be removed when the contact-pin rests upon the tissue. Where the contact-pin comes in contact with the tissue the tip is coated with paraffin.

The brass element is held vertically by means of an attached rod, raised from or lowered into position by the pinion head, and turned about the long axis of the rod by means of a knurled head fitted to the top of the rod. The device thus supported is clamped, beside others, to a horizontal rod above the heart-trough. The element is lowered until the contact-pin comes to rest upon the upper surface of the

heart-tissue, the stop is removed from position and the element adjusted to the level which will give the desired optical deflection.

TUNING-FORK CURVES: Time intervals in conjunction with the above devices are measured with an electrically actuated tuning-fork, with a small mirror (such as is used with the muscle elements) on one arm of the fork. To avoid changing forks for different frequencies a fork has been used with calibrated heads for 40, 50, 60, 80, and 100 double vibrations per second.

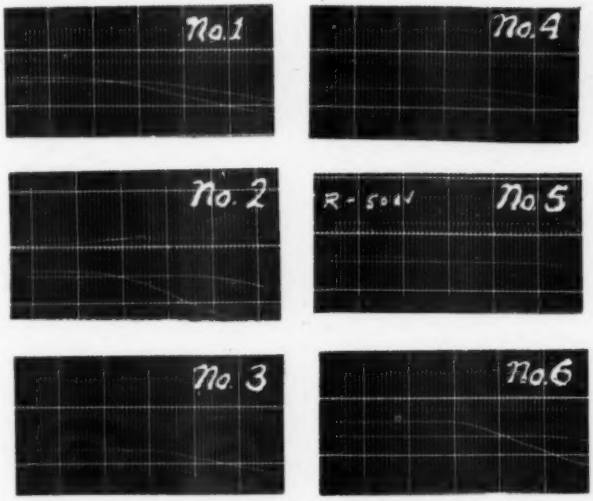

FIG. 3

RECORDING DEVICE: The optical devices are employed in connection with an arc lamp and simple camera by which curves are permanently recorded. An arc lamp of the stereopticon type is arranged with a light tight, ventilated, steel housing with an opening in the front wall closed by an aluminum shutter arranged to be operated electrically. A metal plate back of the shutter has three parallel adjustable slits which coincide with rectangular apertures in the aluminum shutter when the electrical circuit is closed; permitting the use of mirrors on three levels and uniform illumination with one lamp.

A simple camera has been assembled from a kymograph adjustable to different drum-speeds, in a light-proof wooden box fitted with plane shutter operated electrically by contacts on the kymograph shaft. The kymograph (a Wm. Gaertner, spring-motor, model) has a range of speed such that the surface moves between 24.4 and 0.23 cm. per sec.,

or 1.6 to 168 seconds for each revolution of the drum. In use a strip of film two or more inches in width and about twenty inches long is clipped to the surface of the drum. For use with rapidly contracting tissues the shaft of the kymograph is fitted with two knife-edge roller-contacts so that (a) in each revolution of the drum the camera shutter would be opened and closed at desirable points with reference to the contraction-wave, or (b) only one contact could be used to indicate (as by a signal light) the beginning of the film strip.

MUSCLE RECORDS: To further illustrate the recording apparatus one experiment is reported with the records from a strip of turtle heart muscle. The investigation in which these experiments were made has been reported earlier.[2]

Fig. 3 comprises six records of the contraction of a strip of turtle ventricle in Ringer's solution and mixtures of Ringer with isotonic sugar solution. The proportion of Ringer's solution is expressed in tenths, thus 0.7R is a mixture of 7 parts Ringer and 3 parts sugar. A constant stream of air through the liquid mixtures was maintained

TABLE 1.

Record	Solution	Conductivity Ringer = 1.00	Velocity cm per sec.	$v/c = k$
1	Ringer	1.00	9.9	9.9
2	0.7 R	0.69	6.0	8.7
3	0.9 R	0.92	6.8	9.8
4	Ringer	1.00	8.8	8.8
5	0.5 R	0.48	4.6	9.6
6	Ringer	1.00	6.5	6.5

throughout the experiment, the temperature was nearly constant at 20°C., and the hydrogen ion concentration was about pH = 6.8. The points of deviation of the muscle curves with reference to the time curve provide a basis for estimation of the propagation-velocity of the muscle contraction-wave in centimeters per second. The time records are from a tuning-fork vibrating at 50 double vibrations per second. In this case the two muscle curves are from points on the muscle surface 3.0 cm apart, that is, the contraction wave is traveling 3.0 cm. The velocities calculated from the photographic films are recorded in Table 1.

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[2] Jour. Gen. Physiol. *3*, p. 807; 1921.

GENERALIZED MERIDIONAL AND SAGITTAL FORMULAS[1]

By E. D. Roe, Jr.

§1. Introduction

This paper is a mathematical investigation, undertaken at the suggestion of and for the Scientific Bureau of the Bausch and Lomb Optical Company. Its object is to trace the path of a ray from one homogeneous (and isotropic) medium into a second—in connection with the classical idea of an infinitely thin astigmatic bundle as developed by Sturm and later adopted by Abbe, Czapski and others—and especially to determine the tensors or lengths of the conjugate focal distances, the bounding (refractive) surfaces between the two media being of any form whatever.

While such results can be deduced from some formulas of Heath,[2] his derivation of the latter appears to me to be open to mathematical objection from lack of rigor and logical consistency as will be shown, §5. It may also be noted that Culman states in words (without formulas) and without proof and for the case of incidence in a principal plane the nature of the formulas.[3] It seemed to me therefore desirable to derive formulas independently.

Heath starts from what he calls the "Characteristic Function," but it is only an approximation to it, and the developments of this paper show what it is. Later he says two such functions are equal[4] on the boundary between the two media, which certainly differ by an infinitesimal of higher order than the second, and he *neglects* the terms of higher order in placing coefficients equal to zero in the difference of what he says are equals. On the contrary, instead of being *neglected*, these terms of higher order constitute the only logical reason for deriving the writer's results.

The comparison here made is possible because Heath and the writer though starting from different standpoints, subsequently reach a common point of intersection of their paths, at which point comparison can be made. The writer starts from the unquestioned and fundamental proposition of Malus, that if the rays of a pencil in the propagation of

[1] Presented before the Optical Society of America, 26 October, 1922.

[2] Heath, A Treatise on Geometrical Optics, Second Edition, p. 180 et seq., 1895.

[3] Die Theorie der optischen Instrumente, edited by Moritz von Rohr, p. 182; 1904.

[4] Heath, Ibid. p. 182.

light are once perpendicular to a surface, they will always be perpendicular to a surface after any number of reflections and refractions. The surface to which the rays are perpendicular is the wave front surface of propagation of light. Thus if there is a luminous point source in a homogeneous (and isotropic) medium (and the writer's discussion is limited to this kind of media) the surface of the wave front is a sphere, and all the rays are perpendicular to it. After refraction the wave front surface is generally something else, but the refracted rays are perpendicular to it, and this continues to be true after any number of refractions and reflections.

It is not necessary to know the wave front surface in each successive medium. If it is known in the first, all that is necessary for the determinate solution of the problem can be derived for each consecutive medium. Since from the classical point of view[5] we are only concerned with the limit of the point of intersection of two consecutive normals to the surface along a line of curvature (in the case of incidence in a principal section), *that is with centers of curvature, and hence radii of curvature*, it is sufficient to use instead of the equation of the surface itself, the "Indicatrix," or, what may be called from another point of view, the "Osculating Paraboloid" of the surface. This paraboloid, elliptic, parabolic, or hyperbolic is tangent to the surface and has the same curvature and radius of curvature as the surface itself for every normal section through the point of tangency. This property enables us to write down its equation at once, if we know the curvature of the surface. Thus for the Torus, at a point P on the surface, the principal curvatures are known from the principal radii "a" and "a+b sec α," where "a" is the radius of a normal cross section of the ring, "b" is the inner radius of an equatorial section of the ring, and "α" is the latitude of P, the angle from the equator outside to P, measured on a latitude circle (normal cross section). In the case of incidence in a principal plane, §4, 1, we shall use the principal planes of the refracting surface through the point of incidence and the tangent plane to the surface at this point as final XZ, YZ and XY coordinate planes respectively. The geometrical proposition, if the indicatrix is referred to principal planes and the tangent plane at P, the xy term in its equation vanishes, and conversely, applies. The equation of the Indicatrix or Osculating

[5] A possible revolution in this field, as suggested to the writer by Professor J. P. C. Southall, in accordance with the views of A. Gullstrand, is left for future consideration. See A. Gullstrand, Ueber Astigmatismus, Koma and Aberration; Annalen der Physik, *18*, p. 941: 1905.

Paraboloid of the Torus, the axis of Z being positive in the direction away from the convex surface, as in Fig. 1, is accordingly

$$w \equiv z'' + \frac{x''^2}{2a} + \frac{y''^2}{2(a+b\ sec\ \alpha)} = 0,$$

which will be recognized as a special case of formula (1).

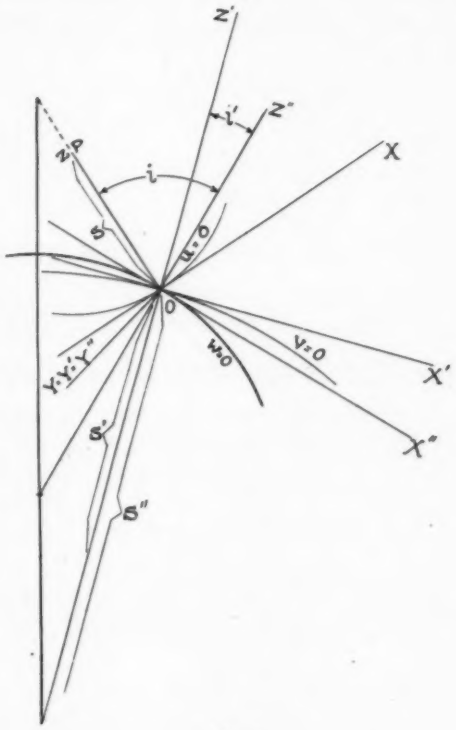

FIG. 1

In Fig. 1, P represents a luminous point source. The principal ray $PO(=ZO)$ is perpendicular to the wave front surface of propagation $u=0$, impinges at O on the refracting surface $w=0$ at the angle of incidence i, is refracted and becomes perpendicular to the wave front surface $v=0$ in the second medium whose normal OZ' (coinciding with the ray in the second medium) makes an angle i' (the angle of refraction) with the normal OZ'' of $w=0$. OX, OX', OX'' are tangent respectively at O to $u=0$, $v=0$, and $w=0$, in the plane of the drawing, (the plane

of incidence), while $OY=OY'=OY''$ is perpendicular to the latter plane at O. Thus we have three systems of rectangular coordinates x, y, z, x', y', z' and x'', y'', z'' with a common origin O, in which $y=y'=y''$ and the first two systems are expressed in terms of the third as shown in Figs. 2 and 3.

XZ and YZ, and XZ'' and YZ'' are principal planes of $u=0$ and $w=0$ respectively and it will be proved that XZ' and YZ' are principal planes of $v=0$, §4, (11).

	x''	y''	z''
x	i	$90°$	$90°-i$
y	$90°$	$0°$	$90°$
z	$90°+i$	$90°$	i

$x=x''\cos i+z''\sin i$
$y=y''$
$z=-x''\sin i+z''\cos i$

Fig. 2

	x''	y''	z''
x'	i'	$90°$	$90°-i'$
y'	$90°$	$0°$	$90°$
z'	$90°+i'$	$90°$	i'

$x'=x''\cos i'+z''\sin i'$
$y'=y''$
$z'=-x''\sin i'+z''\cos i'$

Fig. 3

§2. Equations of the Osculating Paraboloids

In Fig. 1 the principal ray PO is represented as impinging on the *convex refracting surface* at O. Then from what has preceded, R and r being the principal radii of curvature, its indicatrix has the equation

$$w\equiv z''+\frac{x''^2}{2R}+\frac{y''^2}{2r}=0. \tag{1}$$

The case of impingement on a concave refracting surface will be considered in §4, 1, 2). The surface of the wave front in the first medium containing P is a sphere. Its indicatrix at O has the equation

$$u\equiv z-\frac{x^2}{2s}-\frac{y^2}{2s}=0, \tag{2}$$

where s is the tensor or length of PO. The indicatrix of the wave front surface in the second medium on the other side of the refracting surface has the equation

$$v\equiv z'+\frac{x'^2}{2s'}+\frac{y'^2}{2s''}+\frac{x'y'}{2t}=0, \tag{3}$$

where s' and s'' are the radii of curvature of the wave front surface in the second medium in the $X'Z'$ and $Y'Z'$ planes which are later, §4, (11), shown to be principal and meridional and sagittal planes. The coordinates in (1), (2), and (3) refer to the three different before mentioned sets of axes represented in Fig. 1.

Referring the three preceding equations to the same set, x'', y'', z'' of coordinates by means of the transformations in Figs. 2 and 3 and dropping accents, (2), (3) and (1) become respectively

$$u \equiv \left(- x \sin i + z \cos i - \frac{(x \cos i + z \sin i)^2}{2s} - \frac{y^2}{2s} \right) = 0, \tag{4}$$

$$v \equiv \left(- x \sin i' + z \cos i' + \frac{(x \cos i' + z \sin i')^2}{2s'} + \frac{y^2}{2s''} + \frac{(x \cos i' + z \sin i')y}{2t} \right) = 0, \tag{5}$$

$$w \equiv z + \frac{x^2}{2R} + \frac{y^2}{2r} = 0. \tag{6}$$

§3. THE INFINITESIMAL PROPOSITION

It is important to our derivation to note that z, z', z'' in (2), (3), and (1) and therefore their transformed values in (4), (5) and (6) are infinitesimals of the second order or higher as $\begin{vmatrix} x \\ y \\ z \end{vmatrix} \doteq 0$, since they each represent a perpendicular let fall upon the tangent at a point of the curve from a second indefinitely near point of the curve, which is always an infinitesimal of as high an order as the second. We now prove the proposition:

For the coordinates of any point indefinitely near to O and on the surface $z = f(x, y)$, where the axis of z is normal to the surface at O, and whose tangent plane has therefore the equation $z = 0$, and where therefore $z = f(x, y)$ is infinitesimal of as high an order as the second in the vicinity of O,

$$\underset{\begin{vmatrix} x \\ y \\ z \end{vmatrix} \doteq 0}{Lim} \frac{u}{v} = \underset{\begin{vmatrix} \epsilon \\ \epsilon' \end{vmatrix} \doteq 0}{Lim} \frac{- \sin i + \epsilon}{- \sin i' + \epsilon'} = \frac{\sin i}{\sin i'} = \frac{n'}{n}, \tag{7}$$

where n is the index of refraction in the first, and n' that in the second medium.

This follows from substituting the coordinates x, y, z of the point on the surface $z = f(x, y)$ in u and v and dividing numerator and denominator by x and noting that all such expressions as $\frac{z}{x}, \frac{x^2}{x}, \frac{xz}{x}, \frac{z^2}{x}, \frac{y^2}{x}$ are infinitesimal, and the sum of these multiplied by their coefficients in the numerator is the infinitesimal ϵ which approaches zero as a limit, and similarly for ϵ' in the denominator.

By the theory of limits if $lim\ x=a$, then $x=a+\eta$(η infinitesimal) and hence

$$\frac{u}{v}=\frac{n'}{n}+\eta. \tag{8}$$

Therefore $$nu-n'v=nv\eta. \tag{9}$$

u and v are of the second order, therefore $nv\eta$ is of as high an order as the third order of infinitesimals. Hence *when $z=f(x, y)$ is substituted in $nu-n'v$, all terms of the first and second order must vanish.* We may note that the surface $nu-n'v=0$ has contact with the surface $w=0$ at O, since both have $z=0$ for common tangent at this point, as can be found by working out the equation of the tangent plane to $nu-n'v=0$ at the point O. In fact $nu-n'v=0$, $z=f(x, y)$, and $w=0$ all have this common tangent.

§4. Application of the Infinitesimal Proposition

We shall consider incidence in a principal plane both on a convex and a concave refractive surface, and in the same way incidence not in a principal plane.

1. Incidence in a Principal Plane.

By incidence in a principal plane is meant that the plane of the incident ray coincides with a principal plane of the refractive surface.

1). Convex Incidence.

In this case the incident ray impinges on the convex surface of the refracting medium. Applying (9) we have for

$$z=-\frac{x^2}{2R}-\frac{y^2}{2r}$$

from (4) and (5)

$$nu-n'v=[(-n\sin i+n'\sin i')x+\left(-\frac{n\cos i}{2R}-\frac{n\cos^2 i}{2s}+\frac{n'\cos i'}{2R}-\frac{n'\cos^2 i'}{2s'}\right)x^2$$
$$+\left(-\frac{n\cos i}{2r}-\frac{n}{2s}+\frac{n'\cos i'}{2r}-\frac{n'}{2s''}\right)y^2+\left(-\frac{n'\cos i'}{2t}\right)xy+\text{ terms of higher order}], \text{ (along the boundary between the two media).} \tag{10}$$

Since the coefficients of x, x^2, y^2, xy must vanish, we have in the vicinity of O (coefficient of xy) $$\frac{1}{t}=0, \tag{11}$$

that is, of the wave front surface $v=0$, the ZX principal plane of the surface $w=0$ is also a principal plane, and the YZ principal plane of $w=0$ turned through an angle of i' about OY is the other principal

plane, and also s' and s'' are principal radii of curvature and therefore conjugate focal distances. From the coefficients of x^2 and y^2 we have

$$\frac{n\cos^2 i}{s}+\frac{n'\cos^2 i'}{s'}=\frac{n'\cos i'-n\cos i}{R}=\frac{n'\sin(i-i')}{R\sin i}, \text{ (meridional)} \quad (12)$$

$$\frac{n}{s}+\frac{n'}{s''}=\frac{n'\cos i'-n\cos i}{r}=\frac{n'\sin(i-i')}{r\sin i}, \text{ (sagittal)} \quad (13)$$

in which meridional and sagittal are taken to correspond with the plane of incidence and a perpendicular thereto respectively. The vanishing of the coefficient of x is passed over, as it only gives the law of refraction, already used in deriving (9) from (7) and (8).

2). Concave Incidence.

In this case the three indicatrices or osculating paraboloids have the forms,

$$u\equiv\left(-x\sin i+z\cos i-\frac{(x\cos i+z\sin i)^2}{2s}-\frac{y^2}{2s}\right)=0, \quad (14)$$

$$v\equiv\left(-x\sin i'+z\cos i'-\frac{(x\cos i'+z\sin i')^2}{2s'}-\frac{y^2}{2s''}+\frac{(x\cos i'+z\sin i')y}{2t}\right)=0, \quad (15)$$

$$w\equiv z-\frac{x^2}{2R}-\frac{y^2}{2r}=0, \quad (16)$$

since all three would be concave towards the positive directions of their normals as positive directions of the three axes OZ, OZ', OZ''.

Hence while (11) remains unchanged, (12) and (13) become

$$\frac{n\cos^2 i}{s}-\frac{n'\cos^2 i'}{s'}=\frac{n'\sin(i'-i)}{R\sin i}, \text{ (meridional)} \quad (17)$$

$$\frac{n}{s}-\frac{n'}{s''}=\frac{n'\sin(i'-i)}{r\sin i}, \text{ (sagittal)} \quad (18)$$

We also see that (17) and (18) may be taken as the general formulas in the case of incidence in a principal plane of the refractive surface, provided s is taken as negative for convex and positive for concave incidence.

These results for the sagittal formulas (13) and (18) may be confirmed in the special case of refraction at a spherical surface in a very simple way. Figures 4 and 5 represent such refraction. In them s as well as s'' is taken positive for both figures. From Fig. 4, concave incidence, by similar triangles, we have

$$\frac{s\cos i-r}{s\sin i}=\frac{s''\cos i'-r}{s''\sin i'}, \quad (19)$$

or reducing by $\frac{\sin i}{\sin i'}=\frac{n'}{n}$, $\quad \frac{n(s\cos i-r)}{s}=\frac{n'(s''\cos i'-r)}{s''}$, (20)

whence $\quad \frac{n}{s}-\frac{n'}{s''}=\frac{n\cos i-n'\cos i'}{r}=\frac{n'\sin(i'-i)}{r\sin i}$. (21)

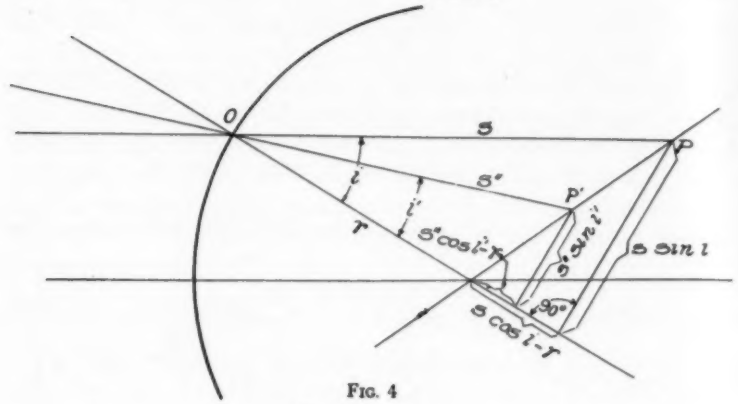

FIG. 4

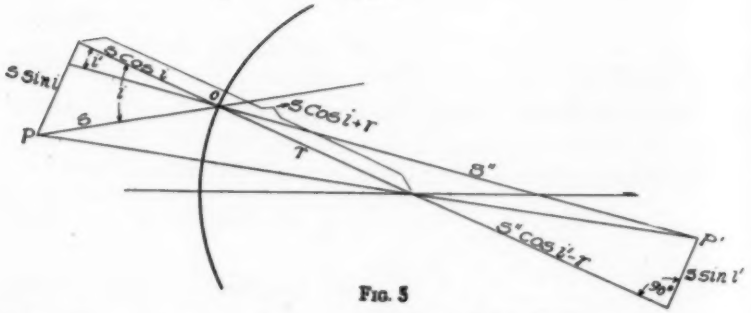

FIG. 5

From Fig. 5, convex incidence, $\frac{s\cos i+r}{s\sin i}=\frac{s''\cos i'-r}{s''\sin i'}$, (22)

which reduces to $\frac{n}{s}+\frac{n'}{s''}=\frac{n'\cos i'-n\cos i}{r}=\frac{n'\sin(i-i')}{r\sin i}$. (23)

It is clear that (23) and (21) are special cases of (13) and (18).

2. Incidence not in a Principal Plane of $w=0$.

1). Convex Incidence.

Let the plane of incidence make an angle β with the YZ principal plane of $w=0$. Then taking the plane of incidence as new YZ plane and the new XZ plane perpendicular to the new YZ plane, the osculating paraboloids have the forms,

$$u \equiv \left(-x \sin i + z \cos i - \frac{(x \cos i + z \sin i)^2}{2s} - \frac{y^2}{2s} \right) = 0, \tag{24}$$

$$v \equiv \left(-x \sin i' + z \cos i' + \frac{(x \cos i' + z \sin i')^2}{2A} + \frac{y^2}{2B} + \frac{(x \cos i' + z \sin i')y}{2C} \right) = 0, \tag{25}$$

$$w \equiv z + \frac{x^2}{2R'} + \frac{y^2}{2r'} = 0, \tag{26}$$

where $R' = \dfrac{Rr}{r \cos^2 \beta + R \sin^2 \beta}$, $r' = \dfrac{Rr}{r \sin^2 \beta + R \cos^2 \beta}$. (27)

Then as before forming $nu - n'v$ and equating to zero the coefficients of the terms of the first and second order, we have, omitting details,

$$\frac{1}{C} = \frac{\sin \beta \cos\beta (R - r) \sin(i - i')}{\sin i \cos i}, \tag{28}$$

$$\frac{n \cos^2 i}{s} + \frac{n' \cos^2 i'}{A} = \frac{n' \sin(i - i')}{R' \sin i}, \tag{29}$$

$$\frac{n}{s} + \frac{n'}{B} = \frac{n' \sin(i - i')}{r' \sin i}. \tag{30}$$

2). Concave Incidence.

The formulas (29) and (30) can be used if s is taken as negative in them, that is, if s is changed into $-s$ in them. The formulas (28), (29) and (30) serve to trace the path of a ray in the second medium after refraction. The geometric and optical significance of A, B, and C is left for study in a future paper.

§5. THE NEGLECTED TERMS

The terms of higher order in (10) which Heath neglects, but which, if nu is equal to $n'v$ along the boundary between the two media as he asserts (I use a different notation from that of Heath, my nu and $n'v$ being identical with his V and V', etc), must also have vanishing coefficients in the difference $nu - n'v$, and thus the equality of nu and $n'v$, taken as premise leads in our case to the following absurdities: The terms of higher order in $nu - n'v$ are

$$+\left(-\frac{2n \cos i \sin i}{2s} - \frac{2n' \cos i' \sin i'}{2s'} \right) xz + \left(-\frac{n \sin^2 i}{2s} - \frac{n' \sin^2 i'}{2s'} \right) z^2$$ and by

equating their coefficients to zero, we get,

$$\frac{n \sin 2i}{s} = -\frac{n' \sin 2i'}{s'}, \tag{31}$$

$$\frac{\sin^2 i}{\sin^2 i'} = -\frac{n's}{ns'}. \tag{32}$$

When $s' = s$, (31) gives $\cos i' = -\cos i$. (33)

(32) gives immediately $\frac{\sin i}{\sin i'} = \sqrt{\left(-\frac{n's}{ns'}\right)}$. (imaginary) (34)

From $\frac{\sin i}{\sin i'} = \frac{n'}{n}$, (32) yields $\frac{\sin i}{\sin i'} = -\frac{s}{s'}$, and $\sin i' = -\sin i$ when $s' = s$ (35)

and by combining (35) with $\frac{\sin i}{\sin i'} = \frac{n'}{n}$, we get $n's' = -ns$. (36)

These absurd results of (33), (34), (35), (36) and others that can be derived serve to show that the premise of the equality of nu and $n'v$ along the boundary between the two media is false, and to emphasize the logical soundness of §§3 and 4, and to justify the criticism here made.

§6. Saddle Shaped Surfaces

The preceding formulas hold for saddle shaped refracting surfaces, it being only necessary to consider and use the proper sign with s according as the section involved is convex or concave, as previously shown in §4.

§7. Circle of Least Confusion

Omitting other details and applications to special cases on account of lack of space, this paper will be closed by giving the distance from O, the point of incidence, to the circle of least confusion, and its radius. Evaluating these according to formulas stated by Heath,[6] we obtain the distance

$$d = \frac{s's''(\sqrt{2s'z} + \sqrt{2s''z})}{s''\sqrt{2s'z} + s'\sqrt{2s''z}} = \sqrt{s's''}, \tag{37}$$

that is, the distance is a mean proportional between s' and s''. The radius

$$r = \frac{\sqrt{2s'z}\sqrt{2s''z}(s'' - s')}{s''\sqrt{2s'z} + s'\sqrt{2s''z}} = \frac{\sqrt{2z}(s'' - s')}{\sqrt{s'} + \sqrt{s''}}. \tag{38}$$

Thus the radius is infinitesimal of the first order, since z is of the second order.

Syracuse University,
July, 1923.

[6] Heath, Ibid. p. 177.

PHOTOGRAPHIC PHOTOMETRY IN THE ULTRAVIOLET

By George R. Harrison and Cedric E. Hesthal

In the course of some work on quantitative absorption in the ultraviolet it became necessary to obtain a more sensitive method of photometry in this region than that furnished by the thermopile. Since all methods of comparing intensities for light of short wave lengths are in a comparatively imperfect state of development, it was determined to investigate the photographic method first, as being in some respects the simplest to handle, and furnishing permanent records.

From the literature on photometry in the ultraviolet it is evident that although a number of papers have been published in which the photographic method was used, it has always been either as a null method, or as an approximation which could be considered valid for certain special cases only, not always easy to reproduce. Also it appears that no work has ever been done on the characteristic curves of plates and films for ultraviolet light, which must be definitely known before great advances in photographic photometry in this region can be made. The present paper is a discussion of some of the difficulties and advantages of the method, with some preliminary results on the characteristic curves of a commercial panchromatic film in this region when developed in elon-hydrochinon. The results are not of particular interest as furnishing definite values, but give an indication as to what may be expected in this region, and clear up certain points which have been uncertain for some time as to the behavior of an emulsion when exposed to light of short wavelengths. All tables and curves given herein refer to the emulsion mentioned above; preliminary work has been done with par-speed portrait film, but the results were not so different as to make a separate discussion of value at this time. Light from 4880 to 2100 A was used.

Photographic photometry in the visible is at best an imperfect subject at present, and in the ultraviolet the same problems hold, with the additional complication that all available light sources are more or less unsteady. By running the filament of an incandescent lamp fitted with a quartz window above normal brightness a fairly constant source can be obtained for part of the ultraviolet.[1] Where a continuous background is necessary, this may be obtained from a mercury arc, a hydro-

[1] Gelhoff, Science Abstracts, No. 431; 1921.

gen discharge tube, a spark between aluminum or tungsten electrodes under water,[2] or exploded wires.[3] In many cases bright lines are of more use than a continuous background, and in the present work the quartz mercury arc was used down to 2500 A, and a spark between cadmium electrodes in air below this region.

None of the above sources are sufficiently steady as ordinarily used, and this is the first important problem of photographic photometry in the ultraviolet. In the present work, the ultraviolet light from the source was partially separated out from the total radiation by a quartz lens with much chromatic aberration and focused on a bismuth-silver thermocouple of the Coblentz type. The mercury arc was run from a 110 volt storage battery of high capacity, and the total light energy was kept constant by a rheostat and air-blower. The radiation from the arc would increase to a certain maximum as it warmed up, and then decrease as the vapor density rose further. It was found that if the rheostat alone was used to keep the total radiation constant, the energy distribution would vary, and therefore it was essential that both current and vapor density remain the same. By controlling the temperature of the quartz jacket with a variable air current both the total radiation and energy distribution could be kept reasonably constant.

In the case of the cadmium spark, which was run from a 1 kw 20 000 volt transformer, steadiness was harder to secure. It was finally attained by having the lower electrode circular in cross section and flat on top, and arranged so that it could be rotated about its own axis freely. The upper electrode was about 1 mm $\times$ 10 mm in cross section, and both were arranged so that the distance between them could be readily controlled without displacing the spark while it was in operation. Light was taken looking at the discharge edge on. A condenser variable by steps was connected across the spark gap, and the latter set at about 3 mm. The capacity was then adjusted so that the spark was steady. The sparks passed at the rate of four for each half-cycle when steadiness was attained, as determined by looking at the gap in a shaking mirror, and the current was adjusted so that it was in the middle of the range where a group contained four discharges. The length of the gap was then adjusted for maximum steadiness as determined by the thermocouple, and then by small adjustments of the primary impedance and closing up the gap as it slowly burned away, with a rotation of the

[2] Howe, Physical Review, *8*, p. 674; 1916.

[3] Anderson, Astrophysical Journal, *51*, p. 37; 1920.

lower electrode frequently, it was possible to keep the total intensity and energy distribution constant to within two or three per cent over long periods of time, by constant attendance on the rheostat, spark gap, and thermocouple galvanometer. The lower electrode was made more massive than the upper because under certain conditions it became so hot as to partially collapse.

Having obtained an approximately steady source of light, the next problem is to vary this light by known amounts, keeping the same relative intensities in all wavelengths. In the visible are available the neutral wedge, the sectored disk, variable apertures, filters, and application of the inverse square law. No neutral wedge has been satisfactorily developed for the ultraviolet, nor have filters been calibrated quantitatively. The sectored disk can be used only in null methods or approximations, since the photographic plate does not integrate in the same way under all conditions. Ultraviolet sources are not adapted to being moved as is the incandescent lamp, nor do they so closely approximate point sources, so the inverse square law cannot be easily called upon. Aperture sizes call for uniform illumination, which again is difficult to attain. Ham, Fehr, and Bitner[4] have used screens of wire mesh, which is equivalent to reducing the aperture and yet does not require even illumination.

In the present work such screens were used. Wire gauzes of mesh ranging from 15 to the inch down to 200 were soldered to brass rings. Those finally used were calibrated very carefully on a radiomicrometer densitometer to within 1 per cent. It was found necessary to frequently recalibrate them, since they could not be counted on to remain constant, especially the very fine mesh, to within less than 5%, even though kept in a covered box. Three were finally chosen as standards, and combinations of these were used in taking all pictures. A set of typical calibrations is given in Table 1. Where combinations of screens were

TABLE 1.—*Calibration of wire screens to total radiation from mercury arc*

Screen No.	Transmission	Rel. Intensity I	$\text{Log}_{10} I$
None	1.000	100	2.00
2	.480	48	1.68
9	.215	21.5	1.33
2+9	.103	10.3	1.01
9+12	.034	3.4	.53
2+9+12	.016	1.6	.21

[4] Ham, Fehr, and Bitner, Journal of the Franklin Institute, *178*, p. 299; 1914.

used they were always placed in different parts of the optical system, and those portions of the beam were chosen where its cross section was greatest.

The purpose being to expose the film to light of known wavelength for a known period of time, with intensity variable by known amounts, a Féry quartz spectrograph was arranged as a sensitometer. Light from the source, after passing through the screens, was focussed on a slit about 1 mm wide, the resulting spectrum having lines 30 mm long, each line being of uniform intensity throughout. A shutter was arranged so that seven exposures could be taken on each film, so that seven rectangles of about 1 mm×4 mm were available on every film for each wave length to be measured. Exposures were timed to a telegraph sounder connected to a standard clock beating seconds, and since the minimum exposure was four seconds, these were in general reliable to less than two per cent, and in most cases to well within one per cent.

Each film contained seven complete spectra taken for identical times but with different light intensities, or else taken for constant intensity but for different times of exposure. The films were developed in a standard elon-hydrochinon solution for five minutes at 20° C., and when fixed and dried were measured on a densitometer which gives densities to within one per cent, described in a recent issue of this Journal.

PHOTOGRAPHIC CHARACTERISTIC CURVES

If an emulsion be exposed to monochromatic light, the resulting density will depend upon the character of the emulsion, the developer used, the process of development, the wavelength of the light, its intensity, and the time of exposure. In the present work all of these factors have been kept as nearly constant as possible with the exception of the last three, which are the variables to be considered.

The opacity of the film being the ratio of incident to transmitted light, while the density is the common logarithm of this, the problem is to determine the function connecting d, I, and t. Since such wide limits are used it is most convenient to plot $\log_{10} I$, and $\log_{10} t$.

In the visible region, which is the only one in which this function has been investigated previously, a number of laws have been proposed. The reciprocity law may be stated

$$d = \gamma \log It - c$$

where γ is called the contrast, and the constant c depends upon the speed of

the emulsion. This law supposes doubling the time of exposure to be equivalent to doubling the intensity of the light; it is known to be only an approximation, but holds very well over a limited range under certain conditions. Where it holds, the problem of photometry is comparatively simple.

Schwarzschild's law[6] says that

$$d = \gamma \log It^p - c$$

where p is known as Schwarzschild's constant. It has since appeared that p is not a constant, sometimes being greater than or less than one. Some investigators still hold p to be a constant[6] however, while others find it a function of the intensity.[7]

It has been the custom to plot d against log E, the exposure, where $E = It$. When this is done we obtain the familiar S-shaped characteristic curve. In actual practice, either I or t is generally varied, the other factor being kept constant. If the reciprocity law holds this is legitimate; if Schwarzschild's law holds, the variation of t with I constant will produce a steeper curve than if I is varied with t constant, since the law may be written

$$d = \gamma \log I + p\ \gamma \log t - c$$

and p is generally greater than one.

Helmick[8] found that if the product It was kept constant, while t was varied, he got a curve with a definite maximum when plotting density against log t. This would show p to be a variable.

A number of formulae have been proposed[9] which fit the experimental facts fairly well; the general opinion seems to be that γ, the contrast, p, Schwarzschild's "constant", and i, the inertia of the plate, are all functions of wavelength, emulsion, development, and intensity. The inertia, i, is the intercept on the log E axis of the $d - \log E$ curve; $10/i$ is defined as the speed of the emulsion.

It is evident that the density which a given light intensity will produce depends upon a number of factors. But in photometry we can keep them all constant if necessary, provided we know the function connecting I and d, since our problem is to compare two intensities by the densities they produce.

[6] Schwarzschild, Astrophysical Journal, *11*, p. 89; 1900.

[6] See Mallet, Philosophical Magazine, *44*, p. 904; 1922.

[7] See Helmick, Physical Review, *17*, p. 135; 1921.

[8] Helmick, Physical Review, *11*, p. 372; 1918.

[9] See Helmick, Physical Review, *17*, p. 135; 1921; also Ross, Journal of the Optical Society of America and Review of Scientific Instruments, September, 1920.

If we define as the sensitivity of an emulsion the density produced by a given intensity expressed in ergs, we find that this varies with wavelength. According to Helmick's results[8] it will also vary with the rate of influx of the light, and there will be an optimum rate of flow when the maximum density will be produced by a given quantity of energy.

The object of the present work, then, is to see how the above discussion applies to the region between 4000 and 2100 A; also to see whether the known decrease of sensitivity of an emulsion below 2500 A is due to decrease in contrast, or speed, or both.

Ross[10] has given curves showing the variation of contrast with wavelength in the visible; he found that the contrast was decreasing rapidly in the violet. He mentions that this may be due either to a change in the characteristics of the emulsion to this region, or to a decrease in the intensity of the light used, if contrast is a function of intensity. It has generally been supposed, however, that an emulsion had much less contrast in the ultraviolet than in the visible.

It appeared evident that the best way to get a clear view of the problem would be to plot a three dimensional curve with d, log I, and log t as the variables. From such a surface we can tell at a glance whether or when the reciprocity law holds, whether p is a constant, and so on. Accordingly, sensitometric strips were taken with the idea of constructing such a surface for each wavelength under standard conditions.

TABLE 2. *Densities produced by light of wave length 2144 A of various intensities and for various times of exposure.*

	Density for various intensities					
Time in seconds	1.6	3.4	10.3	21.5	48	100
4	.22	.23	.28	.41	.70	1.05
8	.23	.26	.41	.60	.93	1.40
16	.27	.38	.62	.89	1.30	1.70
32	.34	.55	.92	1.28	1.70	2.02
64	.44	.78	1.26	1.63	1.93	2.26
128	.57	1.03	1.58	1.87	2.19	2.40
256	.67	1.30	1.89	2.04	2.20	2.32

The intensity of the light was kept constant, and seven pictures were taken for 4, 8, ... 256 seconds with no screen; then screen #2 was interposed, and another set of seven exposures was taken, and so on

[10] Ross, Astrophysical Journal, *25*, p. 86; 1920.

for all six screen combinations. In this way 42 points were obtained on the characteristic surface for each wave length. These were later

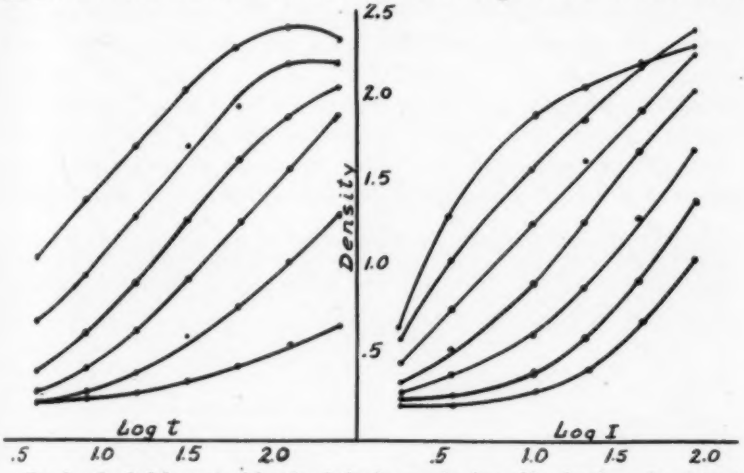

FIG. 1. *On the left, curves giving the relation between density and log time for various intensities of light of wavelength 2144 A. On the right, similar curves giving the relation between density and log intensity for various times of exposure.*

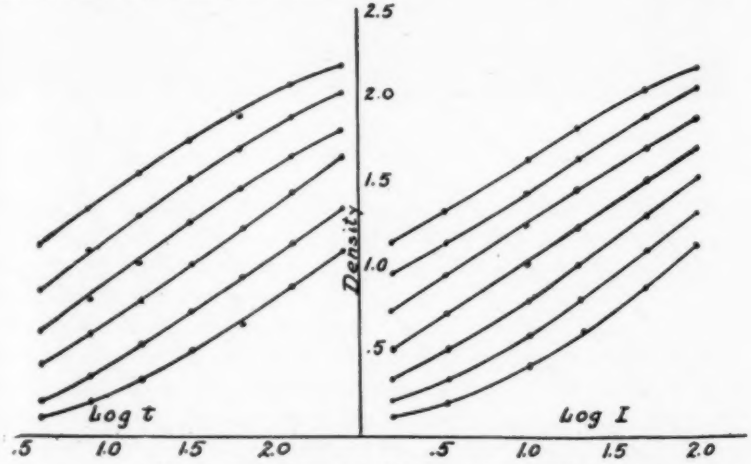

FIG. 2. *Same as Fig. 1, for light of wave length 2350 A.*

checked by taking pictures in which I was varied on each film, with t varying with the different films. A typical set of densities for wavelength 2144 A is given in Table 2.

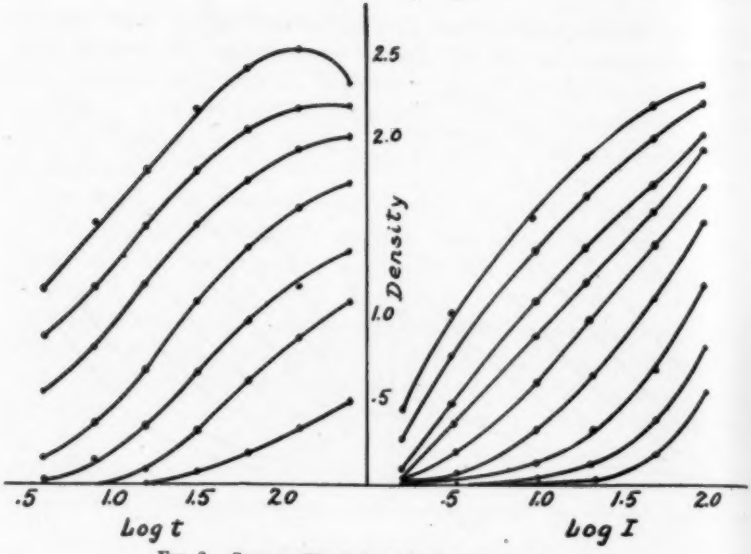

FIG. 3. *Same as Fig. 1, for light of wave length 2730 A.*

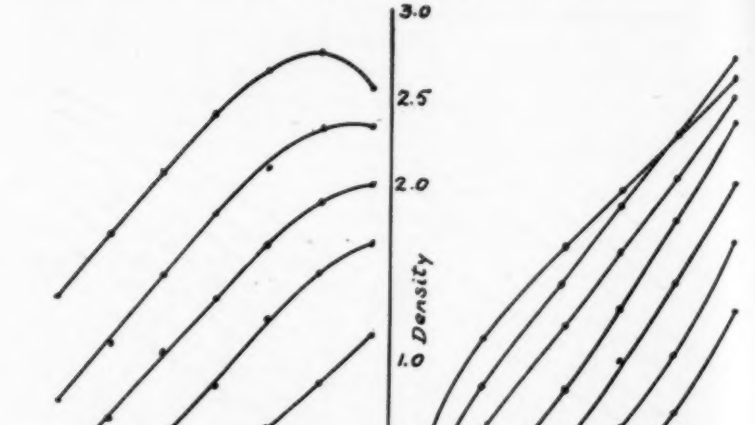

FIG. 4. *Same as Fig. 1, for light of wave length 4840 A.*

These values are shown plotted in Fig. 1, and the succeeding figures show some of the results obtained for other wave lengths. Values were taken for thirteen wave lengths distributed between 4860 A, and 2144 A, but only typical sets for 2144, 2350, 2370, and 4840 A are reproduced.

In Fig. 5 is shown a photograph of three characteristic surfaces constructed from measurements taken. These were made by laying out d-log I curves on boards of uniform thickness, with such a scale that the thickness of the boards was taken as log 2, sawing to these

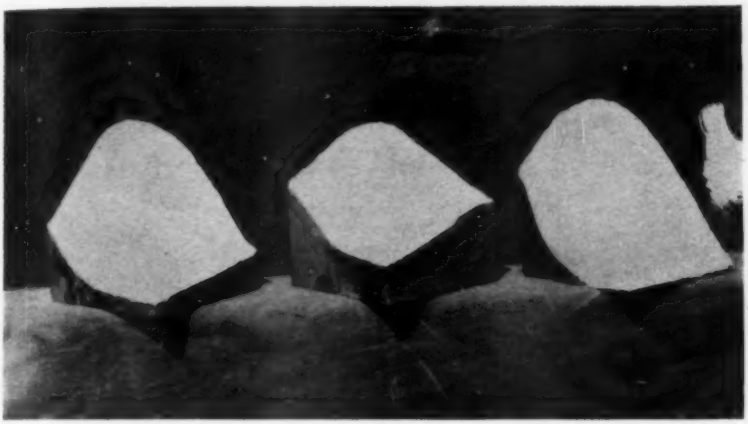

FIG. 5. *Photograph of three "characteristic surfaces" for an emulsion exposed to light of three different wave lengths. On the left, 2144 A, center 2350 A, and right 4840 A.*

curves, and gluing the boards together in the proper positions. The resulting steps in the surface were then filled with beeswax and rosin mixture. This was buffed and smoothed with acetone, and finally painted with white enamel.

If we let $It = \text{const.}$, then $\log It = \text{const.}$ and $\log I + \log t = \text{const.}$ This is a straight line making equal intercepts on the $\log I$ and $\log t$ axes, and if we slice our solid figure along this line in a plane parallel to the d-axis, the resulting intersection gives us an indication of the different densities obtained when various rates of flow are used, It being constant. This curve corresponds to those plotted by Helmick.[8]

In Fig. 6 are plotted a number of such curves taken direct from the data; in some cases the range was not great enough to get a regularly defined maximum, but others show just such characteristics as Helmick

obtained. It is evident that neither the reciprocity law nor Schwarzschild's law holds except under certain special conditions. On the reciprocity law the curves would be horizontal lines; on Schwarzschild's law they would be straight lines with an upward or downward slope, according as p was greater or less than 1.

A comparison of the four families of curves shown in the Figs. 1-4 gives some interesting data in regard to the variation of contrast, inertia, scale, and maximum density with wavelength. It is evident also that we must consider separately the contrast corresponding to the d-log I slope and that of the d-log t slope. The d-log t curve represents the

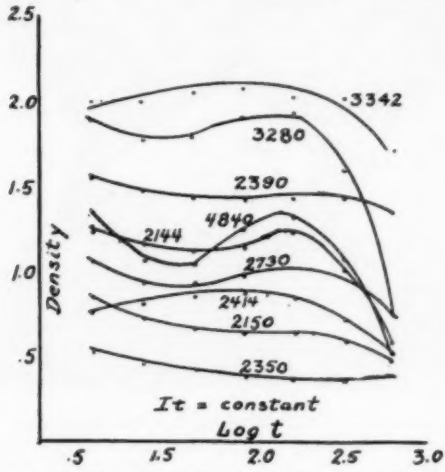

FIG. 6. *Curves showing the relation between density and log time, total energy constant, for the wave lengths marked on the curves.*

actual growth of any image, while the d-log I curves give us the actual basis for comparing images due to light sources of different intensity and hence is of chief interest in photometry. The ratio of these slopes is Schwarzschild's p.

CONTRAST: As the wave length decreases from the visible, if the rate of influx of light energy remains great enough the contrast does not measurably decrease until around 2600 A, when it falls to a very low value at 2350. It then begins to rise again, and by 2144 has reached values as great as those common in the visible.

SPEED: The speed of the emulsion decreases with wavelength, this decrease being very rapid below 2400 A, and being the principal cause

of the decrease in sensitivity noted in this region, attributable to the absorption of the gelatine in the emulsion.

SCALE: The scale of the plate (length of the straight portion of the characteristic curve) varies more with energy input per unit time than with wavelength, although as a whole the scale is less in the ultraviolet.

SCHWARZSCHILD'S p: This can by no means be considered a constant, but the d-log t curve, with It constant, has a maximum which may be more or less flat-topped, in which case $p=1$, or it may have sides of uniform slope, when $p=$constant. This explains the results obtained by previous experimenters, when only limited ranges were used.

MAXIMUM DENSITY: Self-reversal does not set in so rapidly in the ultraviolet as has been supposed, provided sufficient intensity is available. But if we have the same intensities in the visible and ultraviolet, it sets in at lower densities in the ultraviolet.

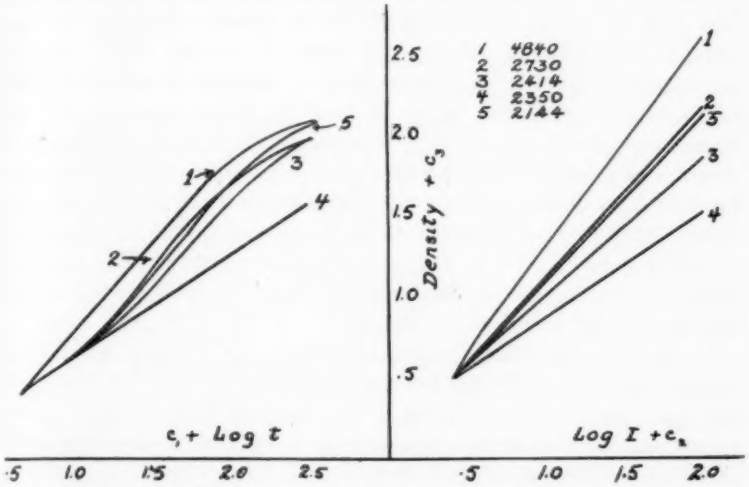

FIG. 7. *Typical density-log time curves on the left, and density-log intensity curves on the right, taken from the central regions of characteristic surfaces for the wave lengths marked.*

In Fig. 7 are plotted a series of curves for different wavelengths, chosen from the central portion of each family of curves, and placed so as to begin at the same point, to show the differences in shape of the central curves.

Throughout this discussion it should be remembered that no attempt was made to measure the actual rate of energy input in ergs per second, and therefore we have no indication of the relative strengths of the

lines used. That is, we may be comparing different portions of the characteristic surfaces in the figures, so far as density produced by a given quantity of energy is concerned. We have one basis of comparison, however, in that we are using the region of maximum contrast in each case, and we are well within sight of the regions of under- and over-exposure. The actual energy needed to produce maximum contrast depends on the threshold sensitivity, and the results show that this decreases with wave length. That is, at 2144 there is a long high plateau more or less gently sloping before the contrasty portion begins; at 4840 this plateau has very little height. This seems to be the most characteristic effect of wavelength.

BATHING OF EMULSIONS IN FLUORESCENT OILS

Duclaux and Jeantet[11] sensitised plates in the region between 2300 and 1800 A., where the absorption by the gelatine decreases the sensitivity tremendously, by bathing them in various oils. Lyman[12] sensitized ordinary plates down to 580 A. by bathing in Nujol, a paraffin oil for medical purposes. If the effect is due to fluorescence, since the fluorescence should be of longer wavelength than the incident light, it would be of interest to see whether the contrast and speed were increased together, or whether only one was responsible for the increase in sensitivity. Hence some characteristic curves of panchromatic film bathed in Nujol were taken. In Fig. 8 are shown several such curves, the dotted lines being for the oiled emulsion, and the solid for the normal emulsion under identical conditions.

At 2144 A oiled film has its opacity/exposure increased as much as 225 times over normal film for high intensities of light. It is evident that the film has greater contrast for light of 2144 A than for the fluorescent light of longer wavelength, although the fluorescence is probably somewhere in the ultraviolet. The greater sensitivity is therefore due to greater threshold sensitivity and speed, which is more than enough to overbalance the decreased contrast.

At 2400 A, on the other hand, bathing the film increases the contrast as well as the speed, but the total sensitivity is not increased so much, the opacity being increased only about four times for the curve shown. The increase in sensitivity for any wavelength is of course dependent upon the rate of flow of energy, the optimum value being obtainable from the

[11] Duclaux and Jeantet, Journal de Physique, *11*, p. 154; 1921.
[12] Lyman, Science, p. 48; July 20, 1921.

two characteristic surfaces of the oiled and normal emulsions. Only Nujol was tried in the present work, this proving satisfactory with panchromatic and portrait film, as well as with other emulsions. Its use is of great value below 2500 A. The films were dipped and allowed to drain a short time, then exposed, the Nujol dissolved in acetone, the acetone washed off with water, and the film developed in the usual manner.

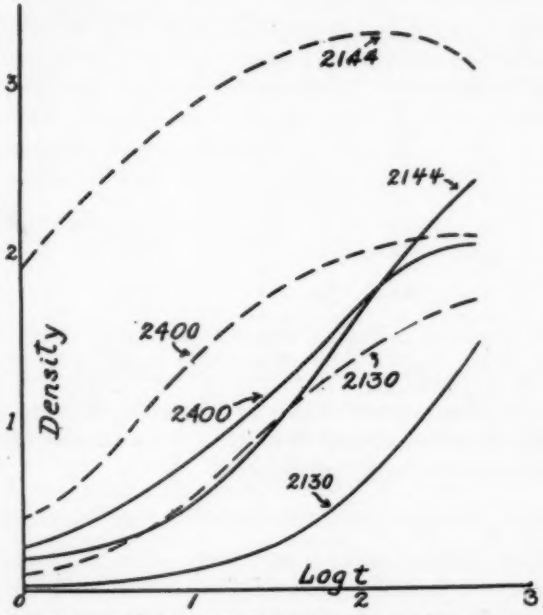

FIG. 8. *Curves showing the change in the characteristic curve of an emulsion produced by bathing it in fluorescent paraffin oil. Dotted curves are for oiled film, while solid curves refer to normal film. For the pairs of curves marked with the same wavelength conditions were identical as far as exposure is concerned.*

Several photographs were taken of the complete spectrum on a film half of which was oiled lengthwise and the other half normal. There was an increase in blackening throughout the spectrum, but very slight and practically constant above 2500 A. This may be due to decreased surface reflection from the film.

In Table 3 are given the ratios obtained for the opacity of an oiled emulsion to that of the normal emulsion exposed under identical conditions. It is evident that the greatest increase in opacity is ob-

tained for shorter wavelengths and for optimum rates of flow of energy, which may be obtained from the characteristic surfaces. Oiling the film is equivalent to pumping the elastic characteristic surface full of air and expanding it, but the elasticity of various parts of the surface depends upon wave length and rate of energy flow.

TABLE 3. *Values of the ratio of the opacity of an oiled emulsion to that of a normal emulsion under identical conditions, for various intensities, exposure times, and wave lengths.*

		Opacity for various times of exposure		
Wave length	Intensity	1 sec.	4 sec.	32 sec.
2130	36	1.2	4.7	5.0
2144	250	20.3	37.0	4.2
2180	39	1.2	4.9	4.4
2195	210	12.6	29.2	4.0
2240	25	1.3	5.3	4.6
2250	26	1.3	4.4	4.2
2265	140	5.1	8.0	3.0
2288	70	1.6	5.0	4.0
2313	210	1.5	2.3	2.6
2350	37	1.05	1.1	1.3
2470	80	1.07	1.08	1.05
2500	85	1.08	1.07	1.08

The subject of treating emulsions with fluorescent oils seems worthy of considerable attention, since it may well solve a number of difficulties in short wave photographic photometry.

APPLICATION OF RESULTS TO PHOTOGRAPHIC PHOTOMETRY

The general problem set may be stated: Given two sources of light of the same wave length, to compare their intensities by the densities produced. If we know the d-log I curve of the emulsion for those wave lengths under standard conditions, this resolves itself into taking two exposures of the same duration, and comparing densities. Where the time of exposure is not the same, we must know the characteristic surface of the emulsion for the wave length considered.

We may thus sum up the problem of photographic photometry in the ultraviolet by enumerating the following individual problems:

1. Development of a steady source of light.
2. Obtaining a standard, uniform, and easily reproducible emulsion suited in sensitivity and contrast for comparison of normal intensities.
3. Deciding on standard and definite conditions of development, such that slight deviations from normal will produce small errors.

4. Knowing the characteristic surfaces of the emulsion for all wave lengths.

If these problems can be satisfactorily solved it will be possible to give the photographic method of photometry in the ultraviolet a wide range, since all that will be required is fulfillment of the standard conditions, an accurate timing device, and a good densitometer to measure within 1%.

The last two conditions are easy to attain. With present methods, however, where each investigator must determine his own characteristic surfaces, the method cannot be recommended where an accuracy greater than 5% is desired. For rapid work where this accuracy is sufficient it is unquestionably the most satisfactory method, especially where much routine work must be done.

STANFORD UNIVERSITY,
CALIFORNIA,
SEPTEMBER 4, 1923.

Further Tests upon Dewar Flasks Intended to Hold Liquid Air. —(For previous paper, see Proc. Roy. Soc. Ed., *41*, p. 97, 1922); An experimental study of the gradual failure of metal Dewar Flasks, containing charcoal in the vacuous space. An ingenious device makes possible the connecting of a McLeod gauge to the bottle without destroying its vacuum. A brass collar into which fits a lead tube "tinned" on the inside with solder, is sealed at some convenient point to the outside of the flask. To the lead tube is attached a long vertical brass tube which is connected to the system containing the gauge. The whole is thoroughly evacuated. Then a sharp-pointed iron rod within the brass tube is allowed to fall from a sufficient height to puncture the external wall of the vessel. In this way actual pressures within the vacuum space, and variations of pressure can be observed. The following are some of the conclusions: (1) In charcoal filled metal flasks, losses due to radiation from outside to inside walls are far more important than losses due to conduction and to connection currents, except for vessels in which the vacuum has suffered great decay, since, when the charcoal is reduced to −190°C the air pressure is reduced in the ordinary case to .001 of its value at room temperature. (2) Neck losses, with a container of usual design, are negligible. (3) Decay of efficacy of such vessels is, in most cases, due to a tarnishing, with consequent increased emissivity, of the interior surfaces. Hence re-evacuation of old vessels is ineffective. (4) Because of the extreme efficacy of charcoal in absorbing residual gas, it is unnecessary in making such flasks to evacuate initially below .1 mm. (5) An improvement can be

made by paying greater attention to means of preserving the luster of the surfaces within the vacuous space. [Henry Briggs, Proc. Roy. Soc. Edinburgh, *43*, pp. 160-169; 1923.]

F. K. RICHTMYER

The Automatic Determination of Ionization Potentials.—This sixteen page article gives in considerable detail directions for the construction and operation of a device for automatically taking the curves necessary in a determination of ionization potential or in fact for any process where a variable voltage must be applied and a corresponding current recorded. A potentiometer is constructed of some two hundred equal coils connected in series to a rheostat and a storage battery of suitable voltage. A rotary switch, driven at any desired rate by a small motor, applies a steadily changing potential difference to the gas under investigation. Attached to an extension of the switch shaft is a drum on which a photographic film is mounted, so that the position of the film is a measure of the applied voltage. The otherwise light-tight case surrounding the film has cut in it, parallel to the axis, a slit, immediately in front of which is located a cylindrical lens. The current to be measured is passed through a galvanometer, from the mirror of which a beam of light is reflected through the cylindrical lens and slit on to the rotating film, thus securing the current voltage curve in rectangular coordinates. A complete run requires two to five minutes.

The potentiometer, film drum, etc., are all mounted on a carriage movable on a track in a direction parallel to the slit in the film drum. By a slight shift of this carriage after each run it is possible to record a large number of curves on a single film. Provision is made for automatically stopping the apparatus at the end of a single revolution and also for marking a scale of voltages on the film by flashing an auxiliary light on and off at regular intervals as the potentiometer switch revolves. [P. Knipping, ZS f. Inst., *43*, pp. 241-256; 1923.]

LEO BEHR